

July, 1936

RUBBER CHEMISTRY AND TECHNOLOGY

Published under the Auspices of the
RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY



VOLUME IX

NUMBER 3

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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, C. W. Christensen, Easton, Pennsylvania, or The Rubber Service Laboratories Co., Akron, Ohio.

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Rubber Division Activities

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Minutes of the Rubber Division Meeting in Kansas City, Missouri, April 15-16, 1936

The meeting was held in the Auditorium. The following papers were presented.

C. S. Fuller. The effect of Vulcanization on the X-Ray Diagram of Gutta-Percha.

F. H. Amon. Changes in Properties and Structure of Carbon Black Accompanying Loss of Rubber Reinforcement Characteristics.

C. W. Walton and H. J. Osterhof. Reinforcement of Rubber by Pigments. III. Comparative Rating of Rubber Gas Blacks by Heat-of-Wetting Measurements.

G. J. Albertoni. Impact Machine for Testing the Tensile Properties of Rubber at High Speed.

Ira Williams. The Pendulum as a Source of Energy for Plasticity Measurements.

The Rubber Division Banquet was held Wednesday evening in the Aztec Room of the Hotel President, with one hundred in attendance. F. W. Frerichs, Chairman of the Entertainment Committee, and F. W. Knoke are to be congratulated for the excellent work which they did in making the banquet a complete success.

A report of the activities of the Crude Rubber Committee was made by Mr. Harold Gray, Chairman of the Committee.

A Papers Committee was then appointed by the Chairman, comprising Ira Williams, Charles Park, and Roscoe H. Gerke.

H. E. Simmons was made an Honorary Member of the Rubber Division for the work which he had done for the Division as its Secretary and Treasurer from 1927 until his resignation in 1934.

The Secretary then made the following report:

Total Membership to April 10, 1936		387
Members paid for 1936	313	
Associate members paid for 1936	74	
New members and Associate members for 1935 (included in above figure)	42	
Total Membership not paid for 1936		126
Members not paid for 1936	97	
Associate members not paid for 1936	29	
New members for 1935 who did not renew membership for 1936	27	
Subscriptions paid for 1936		94
Subscriptions not renewed for 1936	18	
Honorary members and exchanges		30

C. W. CHRISTENSEN, *Secretary-Treasurer*

**Minutes of the Executive Committee Meeting of the
Rubber Division Held in Kansas City, Missouri,
Monday, April 15, 1936**

It was decided that the Rubber Division should meet with the National Society in the Fall of 1936 at Pittsburgh, Pennsylvania.

The Executive Committee was authorized to delegate authority to the Crude Rubber Committee to make necessary decisions with respect to matters that might come within the scope of their activities such as a standard test formula, analytical methods, etc.

The Secretary was relieved of the formulation of the program for the meetings, and this was put in the hands of a Papers Committee consisting of three. The Chair was authorized to appoint the three members for one, two, and three years, respectively, and the succeeding Chairmen to appoint members at the expiration of the appointments.

C. W. CHRISTENSEN, *Secretary-Treasurer*

New Books and Other Publications

Annals of Rubber. Issued by the India Rubber World, 420 Lexington Avenue, New York City. 20 pp.

Consisting of material which has appeared in recent issues of the *India Rubber World*, this booklet is a chronological record of the important events in the history of rubber from 1519 through 1935. It is an interesting compilation and follows the progress of the rubber industry step by step from practically the beginning when it was referred to as a "most singular resin," a description given it by La Condamine. The more important patents granted by various governments are mentioned in the compilation. [From *The Rubber Age* of New York.]

The Rubber Industry. Edited by H. B. Cronshaw. Published by Leonard Hill, Ltd., 17 Stratford Place, London, W. 1, England. 191 pp. 10 shillings.

Described as "an encyclopaedia of all information about rubber, its production, manufacture, and products," this book is a completely revised edition of the book published first in 1930 under the name of "Rubber Information." In addition to revisions, this latest edition includes a 9-page section on latex, describing its source, general properties, colloid characteristics, concentration, production of dipped goods, etc. As in former editions, there are lists of trade and registered names, compounding ingredients and other rubber chemicals, rubber trade statistics, plantation companies, products and equipment, as well as a dictionary of rubber terms. A bibliography of technical books on subjects of interest to rubber technologists is included. [From *The Rubber Age* of New York.]

27th Report of the Rubber Growers' Association. Issued by the Rubber Growers' Association, 19 Fenchurch Street, London, E. C. 3, England. 56 pp.

The activities of the many committees and sub-committees of the R. G. A. for 1935 are contained in this report, which incidentally reveals that the 1153 members, consisting of companies and individuals, control 3,601,000 acres of land approximately 70 per cent of which is planted or inter-planted for rubber. A statement of accounts for the year is included in the report, which also contains a complete list of members. Of specific interest is the report of the Technical Research Committee. [From *The Rubber Age* of New York.]

The American Rubber Industry. By Walter H. Dickerson. Published by the author at 500 Fifth Avenue, New York City. \$25.00.

Prepared in the form of a comprehensive survey for digestion by financial institutions and investors interested in the rubber industry, this book will bring a better understanding of some of the tremendous problems faced by the industry in the last fifteen years, as well as a conception as to the future, which the author regards very optimistically. The survey is in three sections: The Recent History of the Industry; Present Condition of Six Leading Companies; and The Outlook for the Industry. It has many ramifications, briefly discussing each of the more important divisions of the industry, such as tires, mechanical goods, footwear; explaining the failure of the Stevenson plan; lauding the present restriction scheme for its price stabilizing effect; etc. Probably the most important feature of the book to investors is the detailed analysis of the "six leading companies," i. e., in order of size in net working capital, Goodyear, Goodrich, U. S., Firestone, General, and Lee. Comparative earnings, share earnings, sales records, etc., for these companies are shown for the 1925-1935 period in a series of well laid out charts and graphs. All angles of the earning powers of these companies are discussed and commented upon

by the author. A chapter on "General Conclusions and Observations" rounds out the survey and sums up the author's personal opinions as to the future of the rubber industry. [From *The Rubber Age* of New York.]

Rubber Latex. By H. P. and W. H. Stevens. Issued by the Rubber Growers' Association, 19 Fenchurch Street, London, E. C. 3, England. 224 pp.

This is the fourth edition of the book, the first of which was published in 1928. It contains several minor alterations and additions; and the list of patent abstracts, an important part of each edition, has been brought up to date. *Rubber Latex* treats with the properties, composition, coagulation, concentration, manipulation, and compounding of latex and latex pastes, as well as their stabilization for industrial applications. The vulcanization of latex and latex products, dipping, electrodeposition, and the marketing of latex products are also discussed by the authors, both of whom are consulting chemists of the R. G. A. Abstracts of more than 1000 recent British patents on latex and its uses are included in this edition, as is a bibliography of reference books and literature. Copies of the book may be obtained without cost on application to the Rubber Growers' Association. [From *The Rubber Age* of New York.]

The House of Goodyear. By Hugh Allen. Published by The Superior Printing and Lithographing Company, Akron, Ohio. 413 pp. \$1.00 per copy.

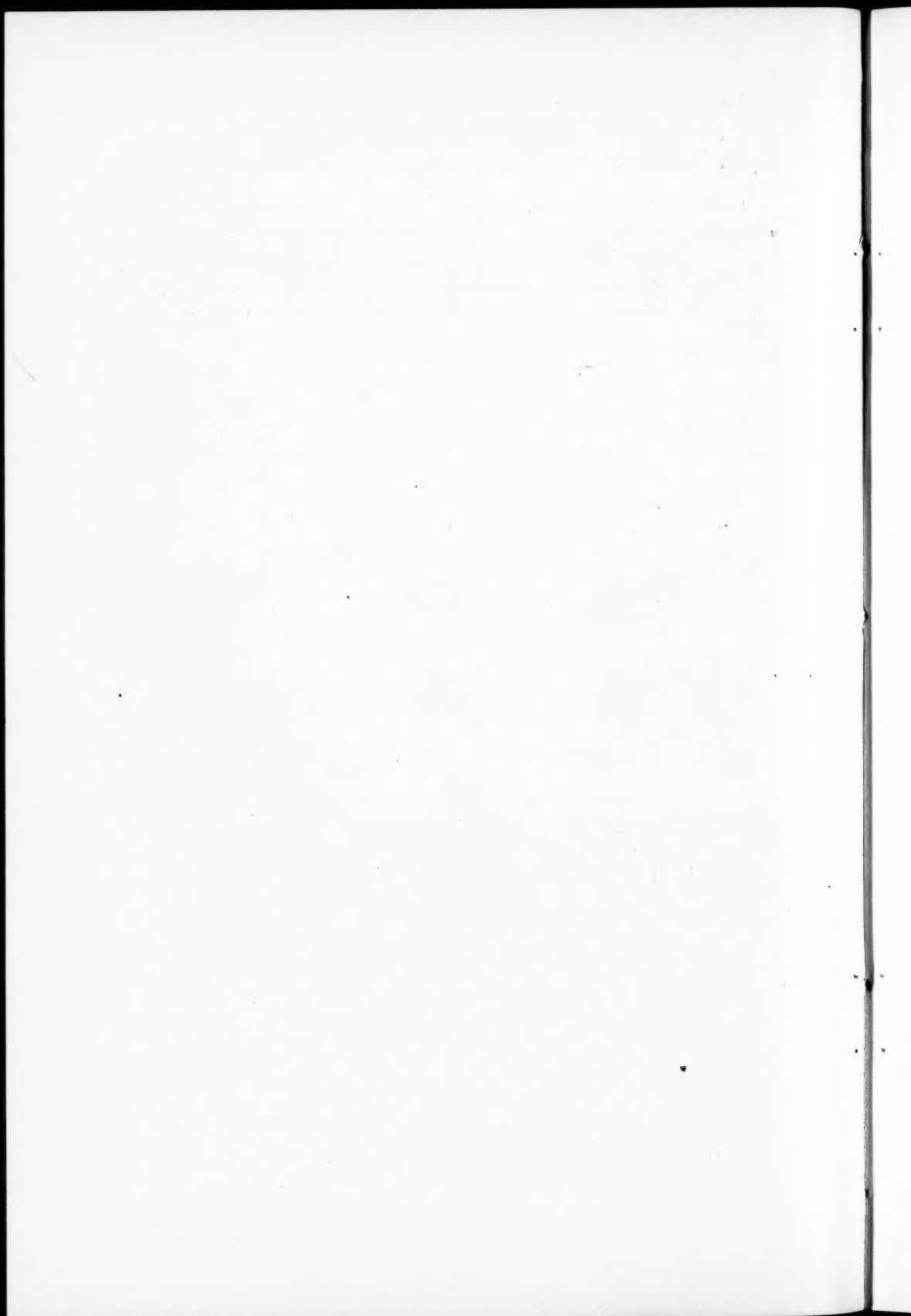
Consisting of 21 chapters and an appendix, *The House of Goodyear* delves into every angle of the company's business, which is so closely allied to the growth of the rubber manufacturing industry of the United States. The early days, development, compounding progress, founding of the Canadian and foreign factories, starting of the Goodyear rubber plantations in Sumatra and the cotton plantations of Arizona, the cotton mills, local expansion—all of these, and more, are treated, with the roles played by individuals associated with each new movement given equal prominence in the telling. A chapter is devoted to Goodyear's part in the development of aeronautics, especially balloons and dirigibles. At the end of the book a chronology appears, as well as a table showing the production facilities acquired by Goodyear in order of their founding or acquisition. A chart showing the fluctuations of crude rubber prices from 1875 to 1935 is also included. This book should be read by every member of the rubber industry, not solely for its tracing of the Goodyear company's fortunes, but for its excellent presentation of the problems of the rubber industry and the accomplishments which turned problems into projects. [From *The Rubber Age* of New York.]

The Chemical Formulary. A Condensed Collection of Valuable, Timely, Practical Formulae for Making Thousands of Products in All Fields of Industry. Volume III. H. Bennett, editor-in-chief. Chemical Publishing Co., Inc., 175 Fifth Ave., New York, N. Y. Cloth, 566 pages, 5½ by 8¼ inches. Indexed. Price \$6, plus postage.

This volume, in the series of practical formulas of which it forms a part, extends the range of information for persons interested in duplicating processes and products developed by experts of some nineteen industries. Each of the nineteen chapters includes more modern formulas in its field than any book on the specific subject. It thus takes the place of nineteen books in the following fields: Adhesives; Paints, Lacquers, Etc.; Cosmetics and Drugs; Emulsions; Farm and Garden Specialties; Food Products; Beverages and Flavors; Inks and Marking Compounds; Leather, Skins, and Furs; Lubricants, Oils, Fats; Materials of Construction; Paper; Photography; Plating; Polishes, Abrasives; Pyrotechnics; Rubber.

Resins, Waxes, Plastics; Soaps, Cleaners; Textiles, Fibers; Miscellaneous Specialties.

Several additional chapters are devoted to tables, references, common names of chemical products, trade named chemicals, and where to buy chemicals. A separate index is supplied, also a combined index for Volumes I, II, and III of the series. The completeness of the formulary is assured by the fact that the data given are ably edited by the editor-in-chief in collaboration with fifty-six chemical experts. The work is invaluable for the chemist and technologist. [From the *India Rubber World*.]



X-Ray Spectrography of Polymers and in Particular Those Having a Rubber-like Extensibility

J. R. Katz

1. Introduction

For many years Staudinger defended the theory that polymers have—in the simplest case—a long chain form of molecules, in which a certain small unit repeats itself regularly along the chain, the units being united by primary valencies. His arguments were not, however, at the beginning of 1927, sufficiently convincing. The decisive argument was forthcoming shortly afterwards by the application of x-ray spectrography. I would like to begin this article by bringing a few personal memories about this development.

At the meeting of the *Naturforscherversammlung* in Innsbruck in September, 1924, I first heard him defend this theory, especially for the case of polyoxymethylenes, but also for some other cases. Neither I myself nor some others to whom I spoke were convinced by his very interesting exposition. His conception seemed possible, but, many of us thought, not proved. And the whole subject did not yet look attractive to many of us.

At the meeting of the *Naturforscherversammlung* in Düsseldorf in September, 1926, where a symposium on high molecular weight substances was held, he again defended this theory. In 1926, the interest in the subject had already increased a good deal, as is clearly shown by the fact that a symposium on the subject had been arranged. Yet, Staudinger's conceptions did not seem to many of us really convincing, nor was the decisive value which x-ray spectrography could have for the subject yet understood at this meeting.¹ Under these circumstances there can be little doubt that the priority of the idea of the long chain molecules for polymers is chiefly due to Staudinger.

At the time this symposium in Düsseldorf was held (Sept., 1926) x-ray spectrography had not yet given the decisive argument as to the form of the molecules it was to give later; it presented on the contrary a new difficulty in understanding them. Mark presented this situation, as it seemed at that moment, very clearly in his lecture for the Düsseldorf symposium.² All the x-ray data collected between 1920 and 1926 showed that the elementary cells of the crystals of all the high molecular weight substances then investigated (cellulose, stretched rubber, silk fibroin, etc.) are small, their weight not exceeding 800 times that of a hydrogen atom. Yet much physico-chemical and chemical evidence points to the fact that these substances, including highly polymerized synthetic polymers, have on the contrary a very high molecular weight, ranging in the tens or hundreds of thousands. It was still doubtful at the Düsseldorf meeting how this fundamental contradiction could be explained.

Some of us who worked on the x-ray spectrography of high molecular weight substances had discussed, as one of the possibilities, the assumption that the molecules might perhaps be very much longer than the elementary cell of the crystals. Polanyi (1921) and Herzog (1921),³ early in the development of the x-ray spectrography of the high molecular weight substances, discussed the possibility of such an

assumption, without however deciding in its favor. I myself in 1924, in writing my first survey on x-ray spectrography of swelling, discussed the same hypothesis.⁴ And in 1925, in describing the x-ray phenomena obtained in stretching rubber, I even made this same assumption as the probable explanation.⁵ Weissenberg discussed the same possibility in 1925.⁶ Yet none of us worked this idea out completely for one substance.

In June, 1926, however, a young California botanist, O. L. Sponsler, made this next step.⁷ In the American Colloid Symposium, June, 1926, held at the Massachusetts Institute of Technology at Cambridge, Mass., he brought a complete picture of the cellulose molecule and how it lies in the elementary cell. He visualized

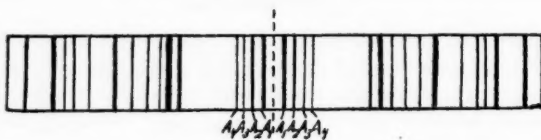
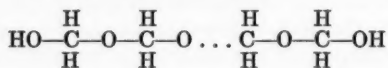


Figure 1

the unit which repeats itself, the $C_6H_{10}O_5$, as a pyranose ring, the side chain $-CH_2OH$ being turned alternately to the left and the right, the unit being joined by primary valencies (glucosidic bindings) to a chain form molecule. This molecule is very much longer than the elementary cell. He described, using Bragg's sphere models, how the carbon and oxygen atoms lie in the elementary cell.

This was the first full picture which showed how to combine the assumption of the long chain molecule with the small elementary cell found by the x-ray workers, and as such has now become a classic, though later Meyer and Mark had to make some changes in Sponsler's picture for cellulose, because they seemed more probable.⁸

Then, in 1927 Mie and Hengstenberg,⁹ working in close collaboration with Staudinger, made the decisive step. (Shortly afterwards, in 1928, Ott, working also with Staudinger's substances, came in principle to the same conclusions.¹⁰) They found the following fundamental facts. The polyoxymethylenes, polymerization products of formaldehyde, have according to the chemical investigations of Staudinger and his collaborators¹¹ the chemical structure:



a chain form molecule ending on both sides in a hydroxyl group. These hydroxyl groups can either be acetylated or methylated and then can show, *e. g.*, by determination of the number of acetyl groups, the length of the chain. It proved to be possible to separate the different polymers from the mixture to such an extent that they seemed to be—on chemical analysis, as specified above—pure chemical substances.

On the other hand, one can determine the length of the chain by x-ray investigations, and show that it increases in proportion to the number of CH_2O groups, determined by the chemical method.

The main x-ray interferences of these different pure polymers are approximately the same, but there are a few central interferences which differ characteristically with the number of CH_2O groups present in the polymer. The authors explained this characteristic fact by assuming that the interferences which are approximately

the same in all the polymers are given by the unit $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{O}- \\ | \\ \text{H} \end{array}$ which repeats itself

regularly along the chain form molecule. The variable interferences measure the length of the chain; they are the different orders of reflection of this length (or of a quantity directly related with it). Figure 1 shows diagrammatically the x-ray pattern of a pure polyoxymethylene diacetate (at random distribution of the crystals). A_1 to A_4 are the first to fourth orders of reflection. The length of the molecule, as calculated from the A-interferences, is shown in Fig. 2. As it is a straight line, the length of the molecule as it lies in the crystalline lattice is proportional to the number of CH_2O units; therefore this molecule must have, in the crystal, approximately the form of a long straight rod. This x-ray result has to be considered as the first direct experimental evidence of Staudinger's hypothesis, and a decisive one. The length of one CH_2O group was approximately 1.9 A. U.

These results were obtained with polymethylene diacetates, and with polymethylene dimethyl ethers. By pressing the material the crystals could sometimes be oriented parallel, and therefore fiber diagrams could be obtained; or the material had primarily the fiber form.

Though in the case of the lower polymers (for instance, with 10 to 20 CH_2O groups) the length of the molecule could be studied, this method failed in the case of the higher polymers. Here it was not possible to separate the polymers into fractions, each having one single chain length.¹² Such complex mixtures now showed a very interesting phenomenon. The small interference rings related with the length of the molecule were failing. This experience is especially interesting, as they have never been found in natural high polymeric substances (like cellulose, rubber) and many synthetic polymers. So we are led to the assumption that, in all such cases where these interference rings fail, there are mixed crystals built up by molecules of such a different length that these interferences cannot be formed. Staudinger at once applied these results to cellulose, asserting that it has in principle the same structure.

The publications of Meyer and Mark in 1928—see paragraph 2—then brought a second experimental evidence for the hypothesis of a long chain molecule, this time of a more complicated nature. The authors worked out its meaning explicitly for cellulose, rubber, chitin, and silk fibroin and made a very important contribution.

The spreading of some high polymeric substances (especially cellulose ethers) in a monomolecular film on a water surface, in films of reproducible thickness and only one hydrocarbon chain thick, which I was able to make in 1928 together with P. J. P. Samwel, may be considered as a third experimental argument for the long chain molecule. The homogeneity of the monomolecular films was doubted; but it was

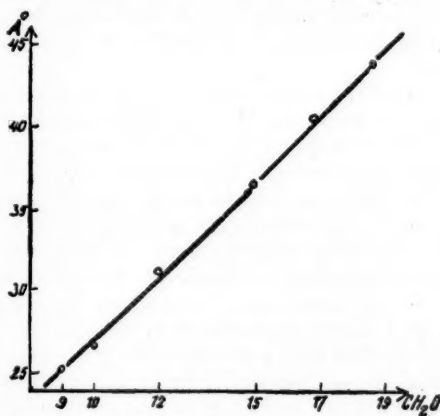


Figure 2

proved to exist in a number of cases by Zocher and Stiebel.¹³ Only their additional research made this experimental evidence fully convincing.

2. The Analysis of Crystalline Patterns of Synthetic Polymers

A number of polymers can show a crystalline pattern; some others have been found only with an amorphous pattern. Some will only give a crystalline pattern when stretched, while they are amorphous in the unstretched form; this latter category we shall discuss later.

There is, however, in principle, no difference in the analysis of a fiber pattern in both cases.

Crystalline polymers are found, for instance, in the case of polyoxymethylenes, polyoxyethylenes, etc. Thiokol (polyethylene tetrasulfide), polychloroprene, polybromoprene, polyiodoprene can be found in the crystalline condition, but also in the amorphous state.¹⁴ Moreover, the polyesters, etc., of Carothers are often crystalline.

In all these cases, when we want to calculate the elementary cell of the crystal, we have to remember the following principles:

(a) When there is a random orientation of the crystals, it is in almost all cases impossible to derive any calculation about the elementary cell.

(b) When we can get all the crystals exactly parallelized, and when they have a sharp lattice, we can get a good fiber pattern. The parallelism can be effected either by stretching or by pressure; in both cases a somewhat plastic condition may be advantageous, or an elastic one in other cases.

(c) In special cases, for instance when stretching very thin films, we may get a higher degree of orientation of the crystals; for instance, not only is a fiber diagram found when such a stretched film is investigated with a primary beam of monochromatic x-rays, perpendicular to the surface of the film, but another regular arrangement will be found when investigated parallel to the surface of the film.

In the case mentioned under (c) there is a higher degree of probability of finding the real elementary cell than in case (b). I have analyzed these facts in my book, "Die Röntgenspektrographie als Untersuchungsmethode bei hochmolekularen Substanzen, bei Kolloiden und bei tierischen und pflanzlichen Geweben."^{14a} It seems unnecessary to give here more than a short outline of the discussion given there. Really certain results can be obtained only with macroscopic single crystals; and those cannot be prepared—it seems now—in the case of most substances of a very high molecular weight.¹⁶

In the cases mentioned under (b) and (c) it is not possible with real certainty to calculate the elementary cell of the crystal; the only thing we can calculate with full certainty is the period of identity in the fiber axis; but the two axes perpendicular to the fiber axis and the angle between them cannot be calculated with real certainty from a fiber diagram (even in case (c)). If one investigates, however, for many years one single substance (as Herzog's school did with cellulose) one can come to a good approximate degree of certainty in the solution one has found. One must be sure to have found all the interferences (including the very weak ones) which can be made visible; one must be certain that they are not due to secondary factors, etc.

The uncertainty of this kind of results in other cases can be best shown by a practical example. Mark—certainly one of the best workers in the field—has calculated together with von Susich the elementary cell of stretched rubber from the fiber diagram, using thin films (see under (c)). He found that the lattice has place for seven isoprene groups, while the number ought to have been eight. In order to

reconcile this contradiction, the authors have to assume that pure rubber has a specific weight 10-15 per cent larger than actually found.¹⁶ All my rubber friends agree with me that such a high specific weight for racked rubber is extremely improbable.

I would, therefore, advise young investigators to be very reticent in undertaking such determinations—unless they are content to get only a probable solution of the problem and in their publication explicitly state so—and not to publish until they have studied many fiber diagrams of their substance made under different circumstances.

The elementary cell once "found" we can proceed to the location of the molecules in it, if the structural formula of the organic compound is sufficiently known. This is a still more delicate procedure than the calculation of the elementary cell. It requires a thorough knowledge of crystallography of organic substances to make a good guess, and often—I am sorry to say—is done without an approximate comparison of the relative intensities of the interferences.

In this way we can come only to a probable solution of the problem and no more. If this is duly emphasized in the publication, nothing is to be said against this procedure. But if it is insufficiently emphasized—as nowadays not rarely happens—then it has the danger of making outsiders give much more credit to these results than they deserve. In this way we are in danger of coming to a construction of results which is not well-grounded and yet materially influences our trend of thought.

On the other hand, it ought to be emphasized that the basic work of this kind on cellulose, rubber, chitin of Meyer and Mark¹⁷ in 1928, and the one on polymethylene diacetate, etc., has been an important service to science.

It must not be forgotten that this work of Meyer and Mark has contributed very much to the present day general acceptance of the conception of the long chain molecules, and that it has brought to light many other new points of view. These researches have shown us what form the molecules of some of the most important high polymeric substances very probably have and how they probably lie in the elementary cells. Especially in teaching the subject, there is a great advantage compared with the situation ten years ago. We then had to tell our students that we did not understand very much about the structure of these substances. That was very discouraging. Now we can tell them, "look here, this is the probable form of the molecule and this is its probable place in the crystalline lattice; maybe all this is not perfectly certain but it is at least a very good first approximation to the truth, an example how things might be." Where the work so relied on is based on pretty solid ground this is a great advantage in teaching. And not only in teaching but in many other cases where application of this picture of the facts proves useful in colloid chemistry or in industry. It gives us at least a first approximative picture of the truth.

3. Results of X-ray Analysis of Crystalline Synthetic Polymerizates

Except for the polyoxymethylene derivatives where Mie-Hengstenberg⁹ and Ott¹⁰ got about the same but slightly divergent results, only a few substances in the group of synthetic polymers have been sufficiently investigated. Here a large field for further investigation lies open. I would draw attention to some interesting conclusions drawn by Sauter out of the x-ray analysis of polyethylene and polymethylene-oxides.¹⁸

Especially promising, I believe, is the group of the polyesters synthesized by Carothers and collaborators, as, *e. g.*, the polyester of sebacic acid and ethylene glycol. As we can systematically vary both the number of carbon atoms of the di-

basic acid and of the dialcohol, we could get a homologous series of polyesters. Here the calculation of the two axes perpendicular to the fiber axis would lead to the possibility of a check on the figures for each of the individual polyesters, by comparison. (Polymorphism would have to be carefully taken into consideration as a possible complication.) Then the results calculated for, let us say, ten or fifteen different polyesters would be far less uncertain than the result calculated for one single term of the series.

The same could be done for analogous substances synthesized by Carothers, Hill, and collaborators, such as polydibasic acid anhydrides, polyamino acids, etc.

This would be a lengthy piece of work, but it might help us, perhaps more than anything else, to understand better than we do now, how much value has to be given to the calculations of the elementary cell and the position of the molecules in it now made for more and more different high molecular weight substances.

4. The Analysis of Amorphous Patterns of Synthetic Polymers

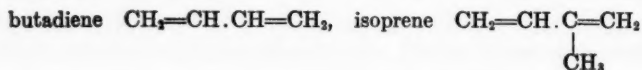
Here the uncertainty of the conclusions is much greater than in the case of crystalline fiber diagrams. But as in that case, an approximative picture of the truth may be gained, if care and discretion is used in applying the method of analysis.

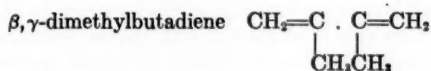
The analysis of the amorphous polymers seems especially interesting in the case of rubber and other substances which "crystallize" on stretching. We shall come back to this question in paragraphs 6 and 7. The "amorphous unstretched rubber" must contain in its "amorphous" structure in some way (at present not understood) a preformation of the highly parallelized and three-dimensionally ordered structure in which the molecules lie when the rubber has been stretched.

This is the reason why I undertook in 1926 the study of the amorphous patterns of rubber and polymers and compared them with the x-ray patterns of about 400 organic liquids. I hoped by comparison of both groups of patterns to find a method of approach for the study of amorphous polymerizates.

Unhappily the results of this research have not yet been duly published. A review of the work done on a part of the large number of organic liquids was published in Dutch in J. Selman's doctor's thesis (Amsterdam, 1932). A short review of our work on organic liquids—in an initial state of the work—was published at the beginning of 1928.¹⁹ Many of the results published there were arrived at independently by G. W. Stewart and by C. V. Raman's pupils. On the other hand, their work corroborates and enlarges our collection of x-ray negatives kept for the analysis of amorphous polymers. We came independently to the same conclusion, that the molecules in a liquid lie in parallel groups—each molecule changing constantly from one group to the other—while the axes of these groups lie distributed at random, and that the average form of the molecule is more rigid than was formerly assumed.

As a matter of fact, I have about 400 x-ray patterns of well-chosen organic liquids to compare with the pattern of the polymers; and this comparison often leads to an analysis of the pattern of the polymer. As a simple example of this kind of analysis, let me give an analysis of the four typical types of polymers described by Harries in 1912 in his classic researches on the polymerization of butadiene, isoprene, and dimethylbutadiene. Butadiene, isoprene, dimethylbutadiene have, as is known, the structural formulas:





These three liquids give x-ray patterns of the same type, the chief amorphous ring having a period of identity, calculated according to the Bragg formula, of

Butadiene	4.6 A. U.
Isoprene	4.9 A. U.
Dimethylbutadiene	5.3 A. U.

Consulting the patterns of the other organic liquids, we can explain what these numbers mean. The distance, 4.65 A. U., is the distance we always find for a liquid having straight, not ramified carbon chains as molecules, if this chain is 4 carbon atoms long or longer (however long it may be). It is the same for hydrocarbons, ketones, alcohols, acids, mercaptans (the other group being attached to one end of the hydrocarbon chain). In the picture to which Stewart, Raman's pupils and I have come, this means that in all these liquids the molecules lie in little groups of parallel molecules, the distance of these parallel molecules in the direction perpendicular to the parallelism being just 4.65 A. U.

Now, if the hydrocarbon or alcohol—having a straight chain of at least four hydrocarbons—has one or two methyl groups as side chains, what do we find? Just such an increase in distance as we have found for the butadienes: 0.3–0.4 A. U. for one methyl group, 0.6–0.7 A. U. for two methyl groups. In the picture of a liquid to which Stewart, Raman's pupils and I have come, this means that the increased distance between parallel hydrocarbon chains in the small groups is 0.3–0.4 A. U. larger for one methyl group, 0.6–0.7 for two.

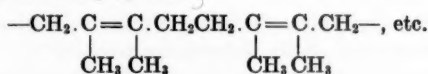
In this picture, the amorphous patterns of the three liquid butadienes are easily understandable.

Now, if these substances polymerize on being heated, what changes happen in their molecules? According to Staudinger, the following substances are formed:

Butadiene thermal polymer— $\text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_2\text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_2\text{—}$, etc.

Isoprene thermal polymer— $\begin{array}{c} \text{CH}_2\cdot\text{CH}=\text{C}\cdot\text{CH}_2\text{CH}_2\cdot\text{CH}=\text{C}\cdot\text{CH}_2\text{—}, \text{ etc.} \\ | \qquad \qquad | \\ \text{CH}_3 \qquad \qquad \text{CH}_3 \end{array}$

Dimethylbutadiene thermal polymer:



What kind of amorphous patterns have these thermal polymers? Practically the same patterns as the liquids from which they were polymerized.²⁰ For the period of identity of the chief ring calculated according to the Bragg formula, we found:

Butadiene thermal polymer	4.6 A. U.
Isoprene thermal polymer	4.9 A. U.
Dimethylbutadiene thermal polymer	5.3 A. U.

An astonishing fact, that these low boiling liquid butadienes have almost the same amorphous pattern as the thermal polymers made from them! But this is just the consequence of the Staudinger formulas; just what one would have to expect on the basis of these formulas. Remember, the distance between the molecules in the groups (perpendicular to the chief chain) is independent of the length of the chief chain, if this is at least four carbon atoms long.

Now, if we make the three other polymers described by Harries in 1912, what do we find? Harries distinguished the following three polymers:

(a) What we now call the *Kondakov polymer* (which grows slowly in the liquid in a form resembling a cauliflower, at room temperature).

(b) The *sodium polymerizate*, made by the interaction of metallic sodium on the liquid butadiene.

(c) The *sodium-carbonic-acid polymerizate*, made by the introduction of metallic sodium in a liquid saturated with carbonic acid.

It was found by him and often corroborated by others that (b) and (c) are very different substances; their ozonides, for instance, split with warm water into very different substances. On the contrary, (a), (c) and the thermal polymerizate show a good deal of analogy to one another.

Now, what does x-ray spectrography show? That the Kondakov and the sodium-carbonic acid polymers have practically the same amorphous x-ray pattern as the thermal polymers, while the sodium polymers have a totally different amorphous pattern, very different from the liquid patterns. This corresponds well to the different splitting up of the ozonides of the sodium polymers observed by Harries and to a number of facts described in later years. The x-ray patterns of the sodium polymers seems to show—by comparison with the patterns of certain organic liquids—that the chief straight carbon chain carries a large number of carbon chains which must be longer than one carbon atom. Some facts from organic chemistry seem to point in the same direction.

In the same way the phenol-formaldehyde polymers might be analyzed by comparison with the liquid patterns of the phenols, especially if the side chains of the phenols are systematically varied. Houwink has already begun to make an investigation of this kind.²¹ Here, as Meyer and Mark first emphasized, the molecule might have the form of a large flat disc.

The more I have had the opportunity to study amorphous polymers of different kinds, either from a scientific or from a technical point of view, the more I have found the comparison with the patterns of a large number of organic liquids a fruitful method. In the course of years one learns to extend one's collection of organic liquids in the direction in which one wants it.²² And generally one is able on this basis to give an interpretation of the amorphous pattern of the polymer.

5. Amorphous Patterns of Synthetic Polymers

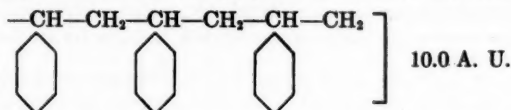
In the case of a number of polymerizations, the amorphous pattern of the polymer is not simply the same as in the non-polymerized liquid. It can be different according to our observations in the year 1927, and in two different ways.²³

(1) Either it is entirely different—as already described for the sodium polymers of the butadienes; this behavior is found in polymerization of vinyl acetate to polyvinyl acetate, or of methyl acrylate to polymethyl acrylate; or

(2) All the interferences of the liquid are found again in the amorphous pattern of the polymer, but one ring of small diameter is added, which I have called the polymerization ring. This behavior is found in styrene-polystyrene; cumarone-polycumarone; indene-polyindene. Liquid styrene, for instance, has an amorphous ring $d = 4.8^{\circ}$ A. U., metastyrene the same ring $d = 4.8^{\circ}$; but, in addition, a small ring $d = 10.0$ A. U. (Figs. 3 and 4). Just so liquid indene has an amorphous ring $d = 5.1^{\circ}$ A. U., while polyindene has the same ring, but in addition a small ring $d = 10.1$ A. U.

It has been difficult, for a long time, to understand the meaning of this polymerization ring. In the case of polystyrene, however, it has been cleared up a good deal

in the course of the last year by the fact that Fuller and I were able—by stretching polystyrene without making it crystalline—to split the polymerization ring into two equatorial maxima.²⁴ This seems to indicate, as in the case of the splitting of the mesomorphic ring of *p*-azoxyanisole in a magnetic field, that the long molecules are oriented by the stretching, with their longest direction in the direction of the stretch. According to Staudinger, polystyrene must have the formula:



The distance between two parallel chains might easily be 10.0 A. U.

In the liquid benzene derivatives, the flat benzene rings probably lie like a roll of coins on one another; we must assume, as all the interferences of the liquid styrene



Figure 3—Styrene

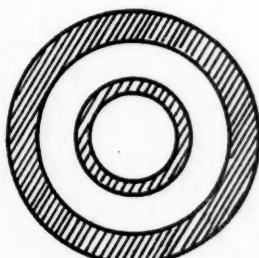


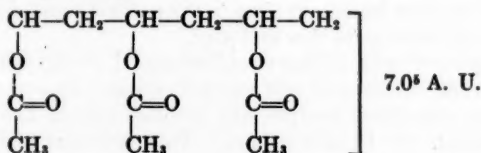
Figure 4—Polystyrene



Figure 5

are found again practically unchanged in the polystyrene, that the flat benzene rings lie very much in the same way in the amorphous polymerization product. But because of the polymerization a new period of identity is found, which we have tried to explain in the way mentioned above.

A very interesting change of the amorphous patterns through stretching is observed when stretching certain samples of polyvinyl acetate. At room temperature they are resinous, at 100° C. the substance is elastic like a piece of rubber. When stretched the substance does not "crystallize," but the inner one of the two amorphous rings develops two equatorial intensity maxima (Fig. 5). This inner ring has a $d = 7.0^5$ A. U. According to the theory of Staudinger the formula of polyvinyl acetate is probably:



As the inner ring develops two equatorial maxima of intensity on stretching, probably the chief chains orient themselves parallel to the direction of the stretch. The distance 7.0⁵ may correspond to the distance between the two parallel hydrocarbon chains. The outer ring $d = 4.0^5$ A. U. is more difficult to explain—perhaps it is the distance between adjacent acetyl side chains.

Queerly enough, many polymers, for instance, isoprene thermal polymer, poly-

methyl acrylate, etc., do not show any change in their x-ray pattern, an amorphous one, when they are stretched. Such substances, once stretched, should, however, be cooled down at once in liquid air and be investigated at its temperature. The relaxation then would be prevented, and we may perhaps observe a change in x-ray pattern which now escapes us.

6. "Crystallization" of Amorphous Rubber when Stretched as a Comparison for Synthetic Substances Which Behave in an Analogous Way

Before describing the x-ray phenomena observed when synthetic polymers with a rubber-like elasticity are stretched, it is necessary to describe shortly the x-ray phenomena which have been observed in the stretching of natural rubber. In these

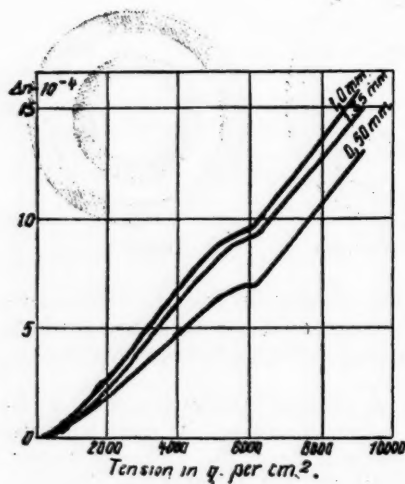


Figure 6

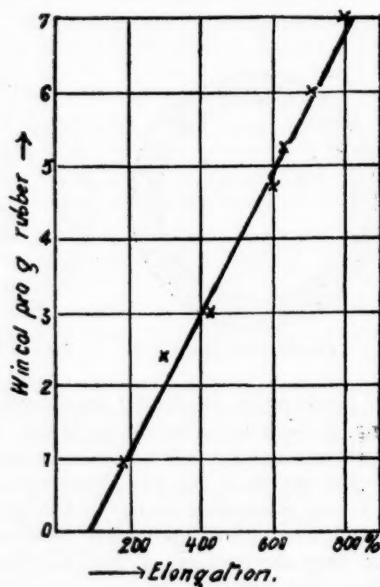


Figure 7

synthetic substances frequently the "crystallization" phenomena are not so fully developed; they are more rudimentary than in the natural substance. We shall in the next paragraph try to indicate how and why.

In 1924, while playing with an ordinary rubber band, I accidentally observed that it was transparent when unstretched and regularly became opaque when stretched. I made a wild guess: something unmixes and becomes opaque like a phenol-water mixture which is cooled. So I made an x-ray experiment and really found that a new "phase," in the sense of the phase rule, was formed by stretching the rubber. This phase is a "crystalline" one, and all the little "crystals" are parallel (with the same crystallographical axis) to the direction of stretch. The x-ray pattern of the unstretched rubber was "amorphous," while that of the stretched rubber was a "crystalline" fiber pattern, superimposed over a weakened amorphous ring.

The fiber pattern shows, moreover, that the rubber must have acquired a fiber structure by being stretched. And that this was the case was also shown by Hock

by freezing the rubber in liquid air and then hammering it; the fissures all lie in the direction of the stretch, while in unstretched rubber they lie distributed at random.²⁴

In stretching the rubber I found there was a critical stretch (about 80 per cent elongation for unvulcanized rubber). A smaller elongation will never produce any "crystalline" interferences; above this critical elongation the intensity of interferences will be the greater, the larger the elongation. In these elongations below 80 per cent the rubber molecules are already oriented in the direction of the stress; but they do not yet "crystallize": they arrange themselves into a three-dimensional lattice.

This "crystallization" I concluded must be the chief component of the Joule heat of rubber, the heat developed by rubber when stretched (as every transition from amorphous to crystalline must give a good deal of heat).

These x-ray phenomena of stretched rubber I first described and developed in two journals which are not much read in England and America.²⁵ My experiments were soon confirmed and further developed by other authors.²⁶

The arrangement and parallelization of the rubber molecules below the critical elongation was investigated at my instigation by van Geel and J. G. Eymers.²⁷ Below the critical elongation the optical anisotropy depends (through an S-form curve) on the elongation; then there is a sharp break, a real discontinuity in the curve; and above the critical elongation the optical anisotropy is strictly proportional to further increase in elongation (Fig. 6).

The heat developed through the "crystallization" is zero till the critical elongation is reached. Then it is strictly proportional to the further increase in the elongation (Hock and Boström).²⁸ (Fig. 7). The intensity of the "crystalline" interferences depends in the same linear way on "the amount of elongation above the critical point" (Hauser and Mark).²⁹

7. Rubber-Like Synthetic Substances Which "Crystallize" when Stretched

(a) *Polyvinyl Alcohol*.—Several amorphous polymers have been studied lately which give a good fiber diagram on being stretched. Polyvinyl alcohol in a certain state of polymerization at a certain temperature was described as giving a perfectly sharp fiber diagram when stretched (F. Halle). A picture of the fiber diagram is given, but further details are lacking in the preliminary publication.³⁰ It would be especially valuable to know if there is a sharp critical elongation, and if curves Figs. 6 and 7 are the same for polyvinyl alcohol as for rubber.

(b) *Polyethylene Tetrasulfide (Thiokol)*.—C. S. Fuller and I studied recently³¹ the x-ray pattern of polyethylene tetrasulfide (Thiokol). From the as yet unpublished article I may quote the following facts. It is generally found "frozen," that is to say, crystalline; it is then hard, brittle, inelastic. When heated above 70° C. it melts, and then becomes an elastic rubber-like substance. It is used in industry because it is a rubber-like substance which is resistant to oil and organic solvents. It is made by interaction of $\text{ClCH}_2\text{CH}_2\text{Cl}$ with Na_2S_4 , and forms a polymer (much in the same way as Carother's polyesters), having the empirical composition $[\text{CH}_2\text{-CH}_2\text{S}_4]_n$, where n is a very large number.

In the frozen condition it has a crystalline pattern; in the unstretched rubber-like form it has an amorphous pattern consisting of two amorphous rings ($d_1 = 10$ A. U., $d_2 = 4.65$ A. U.).

When stretched, the substance behaves like rubber. It then gives a beautiful crystalline fiber pattern, having very sharp interference spots. The identity pe-

riod b in the direction of the fiber axis is 4.32 A. U., or probably double this. Treated with a 10 per cent sodium sulfite solution, one-half of its sulfur is removed. It then has the composition $[\text{CH}_2\text{CH}_2\text{S}_2]$; this has a period of identity in the fiber axis twice as large. We tried to calculate the elementary cell and found as a possible solution a monoclinic space lattice:

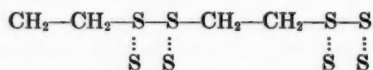
$$\begin{aligned} a &= 8.68 \text{ A. U.} \\ b &= 8.64 \text{ A. U., or } 4.32 \text{ A. U.} \\ c &= 5.03 \text{ A. U.} \\ \beta &= 87^\circ, \end{aligned}$$

in which two, or one group $\text{C}_2\text{H}_4\text{S}_4$ is present per unit cell; these figures have to be taken with all the reserve mentioned in paragraph 2. The unit cell probably has the larger size and contains two $\text{C}_2\text{H}_4\text{S}_4$ units; but no interferences have so far been found in the tetrasulfide, forcing us to make this assumption.

Important evidence can, however, be drawn from the value 4.32 A. U., found for the period of identity in the fiber axis. Two formulas seem possible for the polytetrasulfide. Either it is



or



The x-ray pattern forces us to give up the first formula and to accept the second; the unit of the first is far too long to fit in the dimension 4.32 A. U., while $\text{CH}_2\text{—CH}_2\text{—S.S.}$ just fits in well. The two other sulfur atoms must then be loosely attached, not forming a part of the chief valency chain. This corresponds very well to Patrick's observation, that one-half of the sulfur can be easily removed as by a 10 per cent sulfite solution. This disulfide has an identity period in the direction of the fiber twice as great as the tetrasulfide.

In the polyethylene sulfide series, we have again the same advantage as in the polyester series mentioned in paragraph 3. Instead of ethylene, Patrick has furnished us with methylene or propylene, giving polymethylene tetrasulfide or polypropylene tetrasulfide. If our lattice is well calculated, there ought to be logical changes when comparing these substances. The sulfur content can moreover be made larger or smaller, oxygen can be added, etc., so a good check on the lattices calculated is possible.

We are now working on this program. Determinations of the critical elongation, as in Figs. 6 and 7, have not yet been made, but will be made soon.

(c) *Polychloroprene (DuPrene)* and *Polybromoprene*.—Kenney³² has found that these substances are amorphous in the unstretched condition, while they have a crystalline fiber diagram superimposed over a weakened amorphous ring when it is stretched. The identity period in the fiber axis is 4.9 A. U., showing that we have to do with a *trans*-form like gutta-percha hydrocarbon and not with a *cis*-form like rubber hydrocarbon (the unit would then have an approximate length of 4.1 A. U.).³³ Polychloroprene therefore is a derivative of gutta-percha hydrocarbon and not of rubber.³² The fiber pattern has a characteristic property: while the equatorial interferences are very sharp, the layer line interferences lack sharpness to a varying extent; there is probably some further complication in the problem than we have stated above. I have made many x-ray pictures of these substances, and can corroborate these observations and conclusions out of my own experience. I hope soon to come back to these substances in an explicit publication.

(d) *Methyl Rubber (thermal polymer of β,γ -dimethylbutadiene)*.—This substance gives—as we have shown in 1927³⁴—a fiber diagram on stretching; but this diagram was not fully developed. The sharpness of the fiber pattern depends on the sample of methyl rubber investigated. Hock using another sample did not find any crystallization on stretching when he worked at room temperature, but only when he cooled the sample.³⁵

(e) *Isoprene Rubbers*.—Isoprene rubbers have never given, so far, any sign of crystallization when stretched, not even a change in their amorphous rings. Perhaps, however, they ought to be investigated at low temperature, or better be cooled immediately after they have been stretched.

(f) *The Synthesis of Rubber from Isoprene Has Not Yet Been Made*.—As no isoprene rubber has so far given any sign of crystallization when being stretched; as this "crystallization" on stretching is one of the most characteristic qualities of rubber, I still maintain—as I did in 1926—that the synthesis of natural rubber has not yet been achieved.³⁶ Synthetic isoprene rubber is a different substance from natural rubber. Steinmig was probably right in 1912 when he predicted that natural rubber would never be synthesized, because we cannot achieve a regular sequence of the methyl groups in the synthetic product. In polychloroprene and polybromoprene the activity of the molecules due to the Cl and Br may make this regular attachment more easy. But is the lack of sharpness of the layerlines due to the cause Steinmig indicated, but working to a minor degree? Or to alternations of *cis* and *trans* units? Butadiene rubbers will always be found in forms which crystallize on stretching, as their molecules have no side chains.

(g) *Synthesis of Rubber Ought to Be Done under X-ray Check*.—As the "crystallization" on stretching is a typical quality of any good rubber-like material, the synthesis ought to be worked out so that the material gets a better and sharper fiber pattern on stretch.

Especially for the industrial production of butadiene rubber this may prove, I think, an important method for the improvement of existing types of synthetic rubber. As conditions are forcing more and more countries (*e. g.*, Russia and Germany) to prepare a part of the rubber they need synthetically, this point of view seems to me to be again of considerable importance.

"Crystallization" of rubber or rubber-like substances on stretching is such an extremely characteristic property that where it is defective something essential is lacking in the molecular structure of the rubber (see the next paragraph, however).

8. Spontaneous Crystallization of Natural Rubber and of Synthetic Polymerizates; Their Melting-Point

In addition to the "crystallization" on stretching, both natural rubber and some of the synthetic substances with a rubber-like extensibility show another form of crystallization, this time a real and spontaneous one. When kept at a well-chosen low temperature—different for each substance—its amorphous pattern is changed into a crystalline pattern. At the same time it loses its transparency, becomes hard and inelastic; it ceases to have a rubber-like extensibility. If the amorphous substance is cooled down too far (*e. g.*, in liquid air), it will not crystallize, evidently because the velocity of crystallization has been too much reduced. When the once crystallized substance is heated, it often has a pretty sharp melting-point.

In two cases—natural rubber and Thiokol—it has been shown that the melting interval is quite short. Samples were kept for some time (*e. g.*, a day) in thermostats at constant temperature, then examined shortly afterwards, both with x-ray

spectrography and for specific weight, hardness, and transparency. They were found to have a fairly sharp melting-point, the melting interval being in both cases only a few degrees.³⁷

In the case of natural rubber the melting-point seems to vary with the age of the crystalline rubber; in the case of Thiokol this was not found. In old natural rubber it lies at about 36° C., in Thiokol at about 70° C.

In natural rubber the interesting fact was found that the x-ray pattern formed by the spontaneous crystallization showed the same lattice as the one formed by stretching. This fact makes it difficult to understand why the crystalline pattern once formed by stretching disappears again when the stretched rubber is relaxed.

9. Explanation of the X-Ray Phenomena of Rubber and of Rubber-Like Substances

The following facts have also to be taken into account, before considering an explanation as valid:

(a) *The Substances Which Show Rubber-like Extensibility.*—The organic substances which show rubber-like extensibility seem all to have a long chain molecule. They are:

α. Organic polymerization made of unsaturated compounds: Butadiene rubbers, polychloroprene, polybromoprene; metastyrene; polymeric methyl or ethyl ester of acrylic acid; polymeric vinylacetate; and polyvinyl alcohol.

β. Certain swollen proteins: Gelatin swollen in water, or in water-alcohol, or in water-glycerol; silk fibroin swollen in formic acid; collagen swollen in certain swelling agents; α-keratin, swollen in water, especially after stretching and relaxation.

γ. Perhaps, cellulose, swollen in sodium hydroxide solutions, and certain cellulose derivatives swollen in organic compounds.

Moreover, there are some *inorganic* rubber-like substances, *e. g.*, sulfur and *polymerization products of $PNCl_2$* ; probably these inorganic substances also have a long chain molecule.

(b) *All These Rubber-like Substances Have Some Typical Characteristics.*—α. They develop heat when stretched (like the Joule heat of rubber).

β. They show fiber structure when stretched and frozen in liquid air; the fissures on mechanical treatment all run parallel to the direction of the stretch.

γ. They show, especially when they "crystallize" on stretching, a characteristic stress-strain curve comparable with that of natural rubber.

δ. They show optical anisotropy when stretched, depending in characteristic curves on the degree of stretching.

(c) *In All These Substances the Rubber-like State Exists Only Within a More or Less Narrow Range of Temperature; Swelling Reduces These Temperatures.*—The upper temperature is the one where the elastic substance becomes plastic; it is not generally sharp. The lower limit—called in 1915 by Ostromislensky the "dead temperature"—is the temperature where the rubber changes into a resin. It is accompanied—as Ruhemann and Simon have shown—³⁸ by a large drop in the value of the specific heat; this drop is analogous to the drop in specific heat when liquid glycerin is changed by cooling into a glass. The "dead temperature" again is a temperature interval which, however, may be quite short (*e. g.*, 10°).

If a liquid which swells the rubber-like substance is added, the "dead temperature" is decreased even to a large extent. The *elasticators* of Hofmann (dimethylaniline, dibenzyl ether, etc.) were well known to have this effect in the case of methyl rubber (heat polymerizate of β,γ-dimethylbutadiene). As a matter of fact the

methyl rubber acquired a sufficient elasticity only after the addition of an elasticator. That gelatin, silk fibroin, etc., acquire rubber-like elasticity only after being strongly swollen is again an "elasticator effect," but a very much stronger one than in the case of methyl rubber.

(d) *In the Case of Natural Rubber, the Discontinuity in the Curve of the Optical Anisotropy as a Function of the Elongation Shows That There Are Two Phases in the Stretching of Rubber.*—In the first phase the molecules are oriented into the direction of the stretch and perhaps stretched; but they do not yet form a three-dimensional arrangement. In this part of the curve the optical anisotropy increases according to an S-form curve (as in a nematic phase when its molecules are oriented parallel by a magnetic field); see Fig. 6.

The critical elongation is the stretch, where the initially parallel molecules are forced into a three-dimensional arrangement. As the stretch increases, more and more bundles of molecules are forced into this three-dimensional arrangement, *i. e.*, are forced to reach their critical value.

This formation of crystals may have to do with the characteristic form of the stress-strain curve of rubber, specially with the fact that the elasticity at a certain stretch is almost exhausted. Mallock explained this fact long ago in connection with the resistance of putty to stretching. When the oil film between the chalk particles gets too thin, the putty is not stretched so easily as at first, "it stiffens up."

(e) *Conclusions.*—All these facts have to be explained before we can accept a theory for the rubber-like elastic extensibility as valid. There are two conceptions possible, either we consider the rubber molecule itself as the structure which is stretched and retracts, in which case stretching converts the coiled-up molecule into a straight one, or we assume that the structure which gives the rubber-like extensibility is larger than a molecule.

As the second hypothesis could not be worked out in a good form, we have turned more and more to the first. It would serve to explain the x-ray phenomena on stretching of rubber, and it seems in many other respects probable. But there are two difficulties. One is that we do not see why a rubber once crystallized by stretching should become amorphous again or relax at a temperature far below the melting-point of spontaneously frozen rubber. Secondly, we do not see what force is strong enough to retract the rubber, no matter how carefully we observe. Mack has tried to explain it by the attraction of hydrogen atom to hydrogen atom; others by appealing to the Brownian movement of the chain (Kurt H. Meyer and others). Both conceptions seem possible, but no really convincing argument, I think, has as yet been given. So we cannot yet offer a really good explanation of the rubber-like elasticity and of the x-ray spectrographical facts so closely connected with it.

The same difficulties in the explanation of the x-ray phenomena and the elasticity are met in synthetic substances with a rubber-like extensibility.

References

- ¹ Staudinger, *Berichte*, **59**, 3019 (1926), containing his lecture at Düsseldorf.
- ² See the lecture of Mark, *Ibid.*, **59**, 2982 (1926).
- ³ Polanyi, *Naturwissenschaften*, **9**, 288 (1921); Herzog and Jancke, *Z. Angew. Chem.*, **34**, 385 (1921).
- ⁴ Katz, *Ergebn. exakt. Naturw.*, **3**, 363 (1924).
- ⁵ Katz, *Naturwissenschaften*, **13**, 1411 (1925); *Ergebn. exakt. Naturw.*, **4**, 169 (1925).
- ⁶ Weissenberg, *Z. Kristallographie*, **62**, 13, 52 (1925); *Z. Physik*, **34**, 402, 406, 433 (1925).
- ⁷ Sponsler and Dore, *Colloid Symposium Monograph*, **4**, 174 (1926).
- ⁸ Meyer and Mark, *Berichte*, **61**, 593 (1928).

- ⁹ Staudinger, Johner, and Signer, Mie and Hengstenberg, *Z. physik. Chem.*, **126**, 425 (1927); H. Hengstenberg, *Ann. Physik*, (4) **84**, 245 (1927).
- ¹⁰ Ott, *Helv. Chim. Acta*, **11**, 300 (1928); see later also, *Science*, **71**, 465 (1930); *Z. physik. Chem.*, **9B**, 378 (1930).
- ¹¹ Staudinger, Signer, Johner, Lüthy, Kern, Russidis, and Schweitzer, *Ann. Chem.*, **474**, 145-275 (1929).
- ¹² See, however, Ott, *Z. physik. Chem.*, **9B**, 378 (1930), who studied long chain polymers in which all the molecules seemed to have the same length. In a "paraformaldehyde," *e. g.*, he found a chain length of 60.6 A. U., for a γ -polymethylene oxide one of 113 A. U.
- ¹³ Katz and Samwel, *Naturwiss.*, **16**, 592 (1928); *Ann. Chem.*, **472**, 241 (1929); Zocher and Stiebel, *Z. physik. Chem.*, **147A**, 401 (1930); Adam, *Trans. Faraday Soc.*, **29**, 90 (1932).
- ¹⁴ Thiokol, polychloroprene, polybromoprene can either crystallize spontaneously or become crystallized by stretching. The two kinds of crystals are not necessarily always the same.
- ^{14a} Berlin and Wien, 1934. Urban and Schwarzenberg.
- ¹⁵ Compare, however, the large oxyhemoglobin crystals made by Arthus and others (7 mm. and over), *e. g.*, by alcohol dialysis of a solution in water.
- ¹⁶ Mark and von Susich, *Kolloid. Z.*, **36**, 11 (1928).
- ¹⁷ Meyer and Mark, *Ber.*, **61** (1928), for cellulose, p. 593; for rubber, p. 1939; for chitin, p. 1928.
- ¹⁸ Sauter, *Z. physik. Chem.*, **21B**, 161, 186 (1933).
- ¹⁹ Katz, *Z. angew. Chemie*, **41**, 327 (1928).
- ²⁰ Katz, *Z. physik. Chem.*, **125**, 321 (1927); Katz, Selman, and Heyne, *Kautschuk*, **1927**, 214.
- ²¹ Houwink, *Physik. Eigensch. u. Feinban. v. Natur -u. Kunstharzen*, Leipzig, 1934.
- ²² In recent years B. E. Warren has developed a somewhat different method of analysis of liquid patterns than that which Stewart, Raman's pupils and I have used. The pattern taken up *in vacuo* with purely monochromatic light is analyzed by the photometer and the intensity curve analyzed by Fourier analysis. An application of this method to the analysis of the amorphous pattern of rubber has just been announced (see *Phys. Rev.*, **47**, 808 (1935)), but not yet published at sufficient length to compare it with our concept. It shows in principle that three periods of identity exist in the rubber, the period of 4.9 A. U. mentioned above is interpreted as the shortest distance of a carbon atom from the next carbon atom of an adjacent chain, the two others as intramolecular periods of identity (of a carbon atom to the next, or to the next but one carbon atom of the chain). Warren's method is, I believe, a very promising one.
- ²³ J. R. Katz, J. Selman, and Lottelise Heyne, *Kautschuk*, **1927**, 217; *Z. physik. Chem.*, **125**, 321 (1927).
- ²⁴ Probably Miss M. Hühnemörder (*Kautschuk*, **1927**, 106, 126 has made the same observations as we. But I am not sure that her patterns do not show a change through stretching which goes further than ours, perhaps incipient crystallization.
- ^{24a} Hock, *Z. Elektrochemie*, **1925**, 404; *Kautschuk*, Oct., 1925.
- ²⁵ *Naturwissenschaften*, **13**, 411 (1925); and *Gummi-Zeitung*, **41**, Nos. 36 and 37 (1927).
- ²⁶ Hauser and Mark, *Kolloidchem. Beihefte*, **22**, 88 (1926); Clark, *J. Ind. Eng. Chem.*, **18**, 1131 (1926).
- ²⁷ van Geel and Eymers, *Z. physik. Chem.*, **B3**, 240 (1929).
- ²⁸ Boström, *Kolloidchem. Beihefte*, **26**, 439 (1928).
- ²⁹ Hauser and Mark, *loc. cit.*
- ³⁰ Halle, *Kolloid. Z.*, Dec., 1934.
- ³¹ During my stay as a Baker non-resident lecturer in Cornell University in the first term of 1934-1935.
- ³² See Carothers, Williams, and Kirby, *J. Am. Chem. Soc.*, **53**, 4203 (1931).
- ³³ According to the conception of Meyer and Mark.
- ³⁴ Katz and van Campen, *Chem.-Ztg.*, **51**, 53 (1927). Good pictures of these x-ray patterns in my book, "Die Röntgenspektrographica als Untersuchungsmethode bei hochmolekularen Substanzen," etc., p. 156.
- ³⁵ *Z. physik. Chemie*, **134**, 271 (1928).
- ³⁶ Katz, "Ist die Synthese der Kautschuks schon gelungen?" *Ambronn-Festschrift (Koll. Beih.)*, **1926**, 341.
- ³⁷ For rubber, see Katz and Bing, *Z. angew. Chem.*, **38**, 439 (1925); van Rossem and Lotichius, *Z. Kautschuk*, **5**, 2 (1929); Katz, *ibid.*, p. 8. For Thiokol, see Katz and Bush (not yet published).
- ³⁸ Ruhemann und Simon, *Z. physik. Chem.*, **128**, 1 (1928).

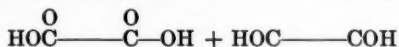
The Formation of High Polymers by Condensation between Metal- lic Polysulfides and Dihalo- genated Hydrocarbons and Ethers

J. C. Patrick

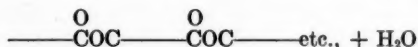
THIOKOL CORPORATION, YARDVILLE, NEW JERSEY

The general theory of formation of high molecular weight linear polymers by condensation between bifunctional compounds of low molecular weight to form products of large molecular mass has been so thoroughly reported in the literature that no extensive citation is believed to be advisable here.

A very thorough study of this type of reaction has been made by Carothers and his co-workers on the formation of polyesters, the reaction being of the general type:



to give



One can, without taxing the imagination, conceive of the polymerization of isoprene or butadiene as belonging to the same general type of phenomenon, differing only in the fact that the reacting molecules are alike instead of different and that the "condensate" is one double bond per molecule. Therefore, no attempt will be made in this paper to distinguish between condensation and polymerization.

When organic dihalides having CH_2X terminals, in which "X" denotes a halogen, are caused to react with metallic polysulfides, MS_xM , there usually results a linear polymer of high molecular weight.



A few specific examples are as follows:

- | | |
|---|--|
| (1) ClCH_2Cl | $+ \text{M}_2\text{S}_x \longrightarrow \text{---CH}_2\text{S}_x\text{CH}_2\text{S}_x\text{CH}_2\text{S}_x\text{---}$ |
| (2) $\text{Cl}(\text{CH}_2)_2\text{Cl}$ | $+ \text{M}_2\text{S}_x \longrightarrow \text{---}(\text{CH}_2)_2\text{S}_x(\text{CH}_2)_2\text{S}_x(\text{CH}_2)_2\text{S}_x\text{---}$ |
| (3) $\text{Cl}(\text{CH}_2)_6\text{Cl}$ | $+ \text{M}_2\text{S}_x \longrightarrow \text{---}(\text{CH}_2)_6\text{S}_x(\text{CH}_2)_6\text{S}_x(\text{CH}_2)_6\text{S}_x\text{---}$ |
| (4) $\text{ClC}_2\text{H}_4\text{OC}_2\text{H}_4\text{Cl}$ | $+ \text{M}_2\text{S}_x \longrightarrow \text{---C}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}_x\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}_x\text{---}$ |
| (5) $\text{ClC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{Cl}$ | $+ \text{M}_2\text{S}_x \longrightarrow \text{---C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}_x\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}_x\text{---}$ |

Many of the linear polymers of the type given above that have been studied either have, or can be readily made to assume, highly rubber-like characteristics.

It will be noted that in the five examples given, Nos. 1, 2, and 3 involve the reaction of a simple hydrocarbon dihalide, whereas Nos. 4 and 5 show the reaction with a hydrocarbon chain containing ether linkages.

Since symmetrical dichloroethane, or ethylene dichloride, may be considered typical of the first type of organic reactant, *i. e.*, the simple hydrocarbon dihalide, its reactions will be given in some detail.

If the polysulfide chosen is a solution of sodium polysulfide properly prepared and having the empirical formula Na_2S_4 , it will react very readily with its equivalent weight of ethylene dichloride in the presence of a dispersing agent such as magnesium hydroxide to form a somewhat latex-like suspension of the polymer. When the suspension of particles has been washed free from the by-products of the reaction by repeated settling and decantation with water, it will coagulate to an elastic rubbery mass on acidification of the liquid.

This polymer is unique in that it shows a degree of extensibility and retractability comparable with natural rubber and also exhibits the Joule effect. According to unpublished observations of J. R. Katz, films of the polymer exhibit an x-ray fiber diagram on stretch comparable with that given by rubber under similar conditions.

Another peculiar analogy with rubber is noted when the polymer is mixed with, for example, zinc oxide and heated. At temperatures customarily used in the vulcanization of rubber, a phenomenon superficially strikingly similar to vulcanization takes place. The originally somewhat plastic mix becomes firm and strongly elastic, and the effect is even more marked if a pigment of the type of carbon black, which exerts such a strongly reinforcing effect on rubber, is present.

Certain suggestions regarding the chemical structure of the ethylene polysulfide polymers will be advanced.

The reaction between ethylene dichloride and sodium tetrasulfide may be represented as:



and



and this process may continue as each new unit is itself bifunctional and capable of reaction at one end or the other, either with a similar unit or with either of the original reactants which happens to be in excess until either or both of the primary reactants is exhausted, after which reaction with chain growth may continue between the already formed units with, however, rapidly diminishing frequency as the average mass of the units increases.

According to the above hypothesis, the polymer would not have chlorine terminals if the polysulfide were kept always in excess, and the empirical formula of the large molecule would approach very nearly to $\text{C}_2\text{H}_4\text{S}_4$. This is confirmed by experimental data.

This hypothesis also postulates high molecular weight, and this is also indirectly confirmed by experiment because, while it has not been possible to determine the average molecular weight of the polymer, all attempts to determine this value have indicated that it is large.

Since there is no good reason to suppose any alteration in the structural relationships of the hydrocarbon residue in this reaction, it will be assumed that the integrity of the $-\text{CH}_2\text{CH}_2-$ radical is maintained. The arrangement of the S_4 complex admits of several hypothetical groupings. One might postulate the polysulfide group extended into a four-sulfur chain in which each sulfur atom is linked to its neighbor or to a carbon atom by a covalent linkage such as $-\text{C} : \text{S} : \text{S} : \text{S} : \text{S} : \text{C}-$, in which each sulfur atom is of equal value as a link in the chain. Another equally valid hypothesis is to assume a configuration for the polysulfide group such as



$-\text{C} : \text{S} : \text{S} : \text{C}-$, in which only two of the sulfur atoms are essential to the integrity of the chain and two others, possibly coordinately linked to the sulfur atoms in the chain might be regarded as likely to considerably modify the physical proper-

ties of the molecule. This assumed structure would lead one to suspect that the two coordinately linked sulfur atoms would be more easily removed than the two sulfurs each covalently linked to carbon, and that their removal, while modifying more or less extensively the properties of the molecule, would not necessarily disturb the fundamental integrity of the chain.

Experimental data show conclusively that in the molecule of $C_2H_4S_4$, two of the sulfur atoms are combined in a very different manner from the other two. For example, if a suspension containing one empirical molar weight of the ethylene tetrasulfide polymer is treated with a solution containing 1.2 mols of sodium hydroxide, and is heated to 80° or 90° C. with agitation for about an hour, the red polysulfide solution of the metal is formed, and when the white somewhat granular residue is washed and dried, its analysis always approaches very closely to the empirical formula $C_2H_4S_2$. If now the disulfide derivative is again subjected to the same treatment with a fresh solution of sodium hydroxide, the polysulfide of the metal, if formed at all, will be present only in minute quantity, and when the organic derivative is removed and analyzed its empirical formula is substantially unchanged.

That the tetrasulfide derivative might have consisted originally of a solid solution of two gram atoms of elementary sulfur in one mol of $C_2H_4S_2$ is disposed of by the fact that extraction with such solvents as boiling acetone does not remove free sulfur and, even more conclusively, by sublimation of the tetrasulfide in a "molecular still" under high vacuum, in which case the empirical formula and physical properties of the sublimate correspond to $C_2H_4S_4$.

As might have been expected, the physical properties of the substance have undergone a change due to the removal of two sulfur atoms from the molecule.

The pale yellow tetrasulfide derivative is elastic and quite rubbery whereas after removal of the two sulfur atoms from the molecule the disulfide is a somewhat harsh granular powder, usually white in color. This powder does not have a definite melting-point. It usually begins to soften perceptibly at around 130° C. and has become a viscous amber-colored liquid at about 180° C., above which temperature evidences of incipient decomposition are observed. That the molecular weight is large is indicated by the fact that the polymer is practically unaffected by any organic solvent. It is not even swollen by carbon disulfide.

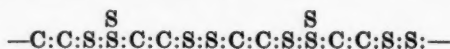
In view of the fact that the removal of two sulfur atoms from each unit of $C_2H_4S_4$ caused a transition in physical properties from a rubbery elastic substance to a granular thermoplastic powder, two interesting questions present themselves. Can the two sulfur atoms be replaced with resumption of all the original rubber-like qualities? Would considerably less than two gram atoms of sulfur per empirical molar weight of $C_2H_4S_2$ suffice to impart rubbery characteristics?

The experimental evidence gives a complete affirmative to both questions.

If one empirical mol of $C_2H_4S_2$ is intimately mixed with two gram atoms of sulfur, especially in the presence of one- or two-tenths of a per cent of an accelerator of the alkaline type (diphenylguanidine is very suitable), and heated for twenty-four hours in an oven at 120° to 130° C., the sulfur recombines and a soft elastic mass is obtained. The same result is produced even more completely if the sulfur and the disulfide derivative are mixed on the rolls of a laboratory rubber mill with, in addition to the accelerator, about 5 per cent by weight of zinc oxide. In this case the mass becomes plastic almost at once but will stiffen to a hard board-like consistency when cold. If now the mix is subjected to a temperature of 145° C. for about thirty minutes, an elastic tough substance resembling cured rubber is obtained. Here also attempts to remove sulfur by the use of selective solvents are not successful.

The answer to the second question as regards the minimum amount of sulfur competent to develop permanently rubber-like properties is easily determined by the last procedure mentioned above. When the disulfide derivative is mixed on the mill rolls with varying proportions of sulfur and the resulting mixes heated as described, it is found that sulfur in the proportion of about one gram atom to two empirical molar weights of the disulfide derivative, that is, an amount of additional sulfur which would give an empirical formula of $C_2H_4S_{2.5}$ suffices to confer permanent rubberiness to the full extent, but that lesser amounts of sulfur are not sufficient.

According to the hypothesis made above concerning the coördinate combination of sulfur, this amount of sulfur would roughly correspond to about one coördinately combined sulfur atom to each two units of the carbon-sulfur chain:



It is interesting to note that the addition of sulfur to form a rubbery elastic substance does not take place under the conditions described above if only one sulfur atom is present in a unit of the chain. For example, polymeric ethylene sulfide, $-CH_2CH_2SCH_2CH_2S-$, does not exhibit this phenomenon.

Attempts to remove more sulfur from the polymeric ethylene disulfide have been unsuccessful without complete decomposition of the molecule. However, in the presence of a suitable reducing agent the S—S bond can be broken. If one empirical molar weight of $C_2H_4S_4$ in suspension in water is first "stripped" of two sulfur atoms with sodium hydroxide solution and, after removal of the polysulfide formed, the mol of $C_2H_4S_2$ remaining is heated with two mols of Na_2S , in solution, to about 90° C. with suitable agitation for several hours, a completely water-soluble product is obtained. A reddish solution of sodium polysulfide is also formed which is found on analysis to correspond to the empirical formula Na_2S_2 . Perhaps:

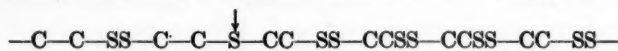


When acidified the aqueous solution obtained by reduction of the ethylene disulfide evolves hydrogen sulfide and eliminates sulfur due to the decomposition of the sodium disulfide. On complete acidification, it also eliminates an oily substance, and on steam distillation a fair amount of ethylene mercaptan is obtained. If now one mol of this mercaptan is treated with the calculated amount of sodium hydroxide solution to form the dimercaptide and the solution of sodium ethylene dimercaptide is then treated with an oxidizing agent such as a sodium tetrasulfide solution or a hypohalite, a substance having most of the chemical and physical properties of the ethylene disulfide polymer, from which the mercaptan was derived, is obtained.

If, instead of acidifying the mercaptide solution, obtained by reduction of $C_2H_4S_2$ with sodium sulfide, the aqueous alkaline solution is filtered and oxidized at boiling temperature by passage of a current of air the identical parent substance is obtained, and when this polymer is treated with additional sulfur in the manner described above the elastic rubbery properties are developed in their entirety.

It is believed that the slight differences noted between the product obtained by oxidation of a pure sodium ethylene dimercaptide, and that derived from the oxidation of the mercaptide solution obtained by first "stripping" then reducing the derivative of ethylene tetrasulfide without prior separation of the mercaptan by distillation, are due to the presence of a certain amount of sodium monosulfide in the

parent polysulfide. This on reaction with $C_2H_4Cl_2$ would lead to the formation of a certain proportion of thioether linkages in the molecule of the polymer:



The chain on reduction may be expected to split only between the $-S-S-$ linkages, with the result that the mercaptide solution should contain in addition to $NaSCH_2CH_2SNa$ also a certain amount of the sodium salt of dimercapto thioether $NaS-C-C-S-C-C-SNa$.

The fact that the rubbery tetrasulfide polymer can be reduced to the disulfide polymer, that this can in turn be reduced to a mixture of mercaptans of fairly well established structure which then by oxidation regenerates the polymeric disulfide, and that the disulfide then can undergo further oxidation with free sulfur to a polymeric tetrasulfide substantially identical with the original polymer, would seem to justify the following inferences:

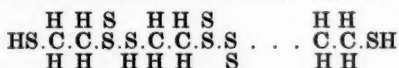
That the fundamental recurring unit in the chain is $-CH_2CH_2SS-$ with an occasional thioether linkage $-CH_2CH_2SCH_2CH_2-$.

That the terminal or end groups after acid coagulation are sulfhydryl groups $-SH$ the same as those of the low molecular weight mercaptans from which the disulfide polymer can be synthesized by oxidation,



That the polysulfide polymers of higher sulfur rank than the disulfide polymer are coordination compounds with sulfur.

A tentative formula for the rubbery tetrasulfide polymer can now be constructed



The experimental data prove quite conclusively that the permanent extension-retraction elasticity, *i. e.*, rubberiness, of the ethylene derivative is dependent upon the presence of not less than a definite minimum excess of sulfur over that required by the empirical formula $C_2H_4S_2$. This excess sulfur is believed to be coordinately combined.

As representative of the dihalides having ether linkages one may select β, β' -dichloroethyl ether for discussion.

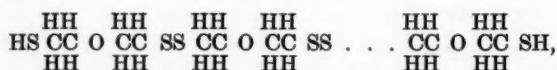
When this dichloroethyl ether reacts with sodium tetrasulfide under similar conditions to those described under ethylene dichloride, a coagulable suspension of the polymer is obtained.

This product shows the analogies with rubber to an even greater degree than is the case with the ethylene derivative.

When the same methods of investigation are applied to the polymeric ether tetrasulfide, as were described in the case of the ethylene tetrasulfide, a very close parallelism can be demonstrated. There is, however, one rather remarkable difference. When the ether tetrasulfide polymer is treated with sodium hydroxide solution until no further sulfur can be removed, the latex-like suspension remaining will coagulate into a white highly elastic mass when treated with acid. This elastic polymer has by analysis the empirical formula $OC_4H_8S_2$. When dried and sheeted out it closely resembles natural rubber in its "liveness." This polymer undergoes a typical vulcanization when compounded with zinc oxide or litharge, and when properly compounded with reinforcing pigment and "cured" it develops a degree of elasticity and resistance to tear fully equal to rubber.

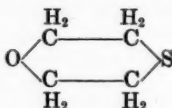
This ether disulfide polymer can be made to take up two gram-atoms of sulfur per mol of $\text{OC}_4\text{H}_8\text{S}_2$ to reform the tetrasulfide polymer, but the addition of sulfur does not in this case enhance the rubber-like properties. The same observation applies in the case of the polymeric disulfide derivative of chloroethoxy chloroether.

The ether disulfide polymer on treatment with sodium sulfide is reduced to mercaptide from which the polymer can be regenerated by oxidation. Therefore similar inferences regarding its structure will be made as were made in the case of the ethylene derivative.

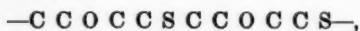


which in the large molecule approaches closely the ratio required by the empirical formula $\text{OC}_4\text{H}_8\text{S}_2$ given by analysis.

It is of interest that in the reaction between polysulfide solutions and β, β' -dichloroether about 15 to 20 per cent of the dichloroether, depending on the type of polysulfide solution used, goes to form the cyclic compound 1-4 thioxane,



The thioxane formation is believed to be accounted for by the presence of monosulfide in the polysulfide solution, since a high yield of thioxane is obtained when β, β' -dichloroether reacts with pure sodium monosulfide solutions. In this reaction only a small yield of the chain polymer,

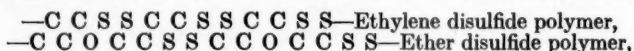


is obtained as a somewhat granular white powder giving no evidence of elasticity whatsoever.

At this point it may be well to compare the probable chemical structure of the unit of the polymers with the gross physical properties in tabular form.

Unit of Polymer	Approximate Physical State
$-\text{CH}_2\text{S}$	Powder
$-\text{CH}_2\text{SS}$	Powder
$-\text{CH}_2\text{SS}-$	Rubber-like
SS	
$-\text{CH}_2\text{CH}_2\text{S}-$	Powder
$-\text{CH}_2\text{CH}_2\text{SS}-$	Powder
$-\text{CH}_2\text{CH}_2\text{SS}-$	Rubber-like
SS	
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$	Powder
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{SS}-$	Powder
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{SS}-$	Rubber-like
SS	
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}-$	Powder
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{SS}-$	Rubber-like
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{SS}-$	Rubber-like
SS	
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}-$	Powder
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{SS}-$	Rubber-like
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{SS}-$	Rubber-like
SS	

In view of the fact that, whereas no rubber-like characteristics were exhibited by the ethylene disulfide polymer but were developed when oxygen was present linked to the beta carbon atom, as in the disulfide derivative of β, β' dichloroether,



investigations are now in progress to determine whether or not the monosulfide derivatives can by any structural rearrangement be made to assume the typical rubber-like properties.

For example, by reacting sodium ethylene dimercaptide with dichloroether, an interesting variation in the sequential arrangement can be made:



This polymer does not, however, exhibit rubber-like properties.

In consideration of the fact that one of the most remarkable properties displayed by several of the polysulfide polymers is their capacity to undergo a change at least superficially analogous to the vulcanization of the diene polymers, a few comments on this phenomenon will be made.

As investigations are now in progress which it is hoped will clear up some of the more obscure points on the subject of "cure" or vulcanization, no extended discussion would be justified.

The heat vulcanization phenomena exhibited by the polysulfide polymers appear to involve in every case an oxidation process. Oxidizing agents such as di- and trinitrobenzene, benzoyl peroxide, etc., promote vulcanization, whereas reducing agents such as pyrogallol and zinc dust greatly retard and in many cases inhibit this process.

A number of metallic oxides are very effective in promoting vulcanization, among which zinc oxide and cupric oxide are perhaps to be preferred. It should be noted also that a trace of moisture in the mix promotes the process.

For example, if the ether disulfide polymer is placed in a mold in a vulcanizing press, the platens of which are heated to 145°C . and the mold is exposed to this temperature for thirty minutes, then cooled and removed, no particular change is observed, except that the material is usually somewhat more plastic than before heating. If the time of exposure to the temperature is increased, a tendency to stickiness of the surfaces of the sample becomes noticeable. If, however, before subjecting to the vulcanizing temperature, 100 parts by weight of the plastic polymer are intimately mixed or compounded with 10 parts by weight of powdered zinc oxide and heated as described, a very different result is obtained. The rather plastic mass has taken the exact shape of the mold, and has developed toughness and "nerve." When a strip of the material is pulled out to an elongation of about 500 per cent of its original length, the piece becomes warm, and when permitted to resume its former length a perceptible cooling effect is noted. If stressed beyond its strength it breaks with a sharp snap.

If the time of exposure to temperature is doubled, the toughness of the material is found to have increased. The ultimate elongation at break has decreased, but the stress required to produce any given deformation (the modulus) has increased. When, in addition to the zinc oxide, about 20 parts by weight of carbon black is compounded with the polymer, all of the physical properties are markedly enhanced.

To show graphically the very marked change in physical properties, and presumably in internal structure, brought about by heating the polymer in the presence of suitable vulcanizing agents, a stress-strain diagram is presented. In this diagram

the loads required to cause a given elongation of the test specimen are plotted against the percentage of the original length represented by that elongation. For convenience points were chosen at 100 per cent elongation and at multiples of 100 per cent and a smooth curve drawn through the points so established. A low tensile soft mixture was chosen, since one of this type shows most clearly the change in shape and the displacement of the curve with increasing time and/or temperature.

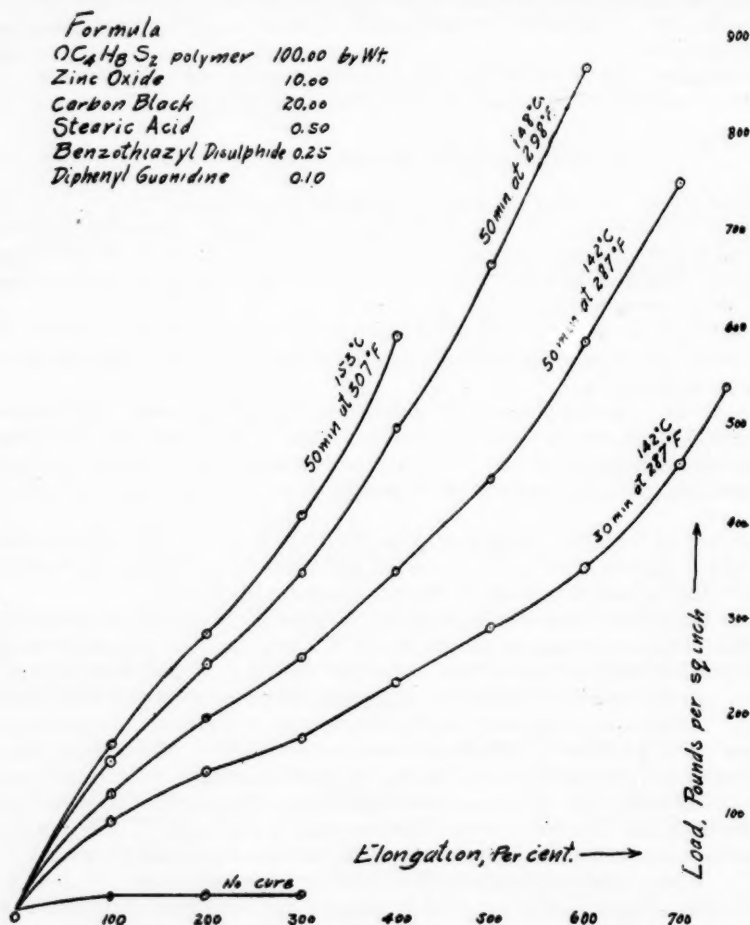


Figure 1

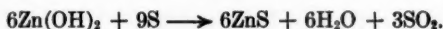
It is of interest to compare the general shape of these curves with the stress-strain diagram deduced on theoretical grounds for rubber by Mack.

The statement was made that the phenomena of vulcanization displayed by polysulfide polymers appear to be caused or accompanied by an oxidation process. Zinc oxide is not, however, ordinarily regarded as an oxidation agent.

Investigation has shown that when any of the vulcanizable polysulfide polymers is vulcanized with zinc oxide, or zinc hydroxide, since traces of moisture are invari-

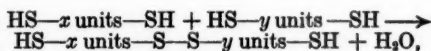
ably present and have in some cases been demonstrated to be essential, a certain amount of zinc sulfide is always present after vulcanization. The exact proportion of zinc oxide changing to the sulfide during vulcanization has not been determined with a sufficient degree of accuracy, on account of the very considerable experimental difficulties attending its quantitative separation from the vulcanized mass.

Obviously then a certain amount of hydroxyl has been replaced by sulfur in combination with the zinc. When zinc hydroxide combines with sulfur a considerable potentiality for oxidation is displayed. For example, when powdered zinc hydroxide is intimately mixed with powdered sulfur and the mixture is heated in a tube, a considerable amount of sulfur dioxide is evolved. The complete reaction may be represented as:



As it has been shown above in commenting on the hypothetical structure of the linear polysulfide polymers, the presence of terminal —SH groups is a very plausible inference from their synthesis from the mercaptans. In a way the polymers may themselves be considered, according to this hypothesis, to be mercaptans of very high molecular weight.

Considered in this way, if it is shown that "vulcanization" of these polymers always involves an oxidation, the thought immediately suggests itself that at the elevated temperatures a further oxidation polymerization takes place and that the "heat vulcanization" of these polymers involves only the raising of the average length of the chain to a higher level. In other words, two chains, one x units in length, and the other y units long, both having —SH end groups may undergo mutual oxidation if a terminal group of one happens to be in juxtaposition with a terminal group of the other to give,



the two original chains having coalesced through an —S—S— linkage to give a similar chain $x + y$ units long.

This simple hypothesis would "explain" all the phenomena of heat vulcanization as due to increase in the average molecular weight or increased degree of polymerization. While it is probable that this hypothesis would account for a part and perhaps a large part of the phenomena of heat vulcanization of the polysulfide polymers, it is also probable that other factors than linear polymerization may play a part. For example, the marked increase in resistance to solvent penetration with increased state of vulcanization would strongly suggest the possibility of cross linkages taking place with a "tying in" of the whole structure.

In the present state of the investigation, no mechanism by which this cross linking might take place can be suggested.

Aside from their scientific interest, several of the elastic polysulfide polymers have furnished the technologist with very valuable tools because, although they strongly resemble rubber in elasticity, capability of reinforcement and modification by pigments, and especially in their ability to undergo "cure" by heat, in which they pass from a fairly plastic workable mass to a tough elastic final form, they differ uniquely from rubber and its cognate polymers in their chemical stability and their resistance to attack by organic solvents and by oxidation.

Certain of these polymers when properly compounded and cured are adaptable for use over a very wide temperature range. For example, compounds have been made which were as flexible at 50° F. below zero as at ordinary temperatures, and

the same compound underwent no appreciable change when immersed in hot lubricating oil for days at 212° F.

In view of the several hypotheses advanced in recent years to account for the extension-retraction elasticity of rubber, it would be of great interest properly to evaluate the significance of the peculiar analogies in physical behavior of many of the polysulfide polymers when compared with the characteristic properties of rubber, because in spite of the obviously very different chemical constitution of the polysulfide polymers, it appears probable that the parallels are so numerous as to rule coincidence out of court, and that a more plausible assumption under the circumstances is that some fundamental structural similarity and spatial relationship obtains.

On the other hand, the very differences in chemical constitution of the rubber-like polysulfide polymers compared with that of rubber and other diene polymers may be of service by shedding an oblique light on the subject of what is necessary in the way of chemical structure and space relationships to cause a molecule to be rubber-like.

I wish to acknowledge my indebtedness to the valuable assistance given by S. Maner Martin, Jr., of the Thiokol Corporation Research Laboratory in carrying out the experimental work to which reference has been made in this paper.

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Chloroprene Synthetic Rubber (Sovprene)

A. L. Klebanskiĭ, L. G. Tzyurikh, and I. M. Dolgopol'skiĭ

The reaction involved in the low-temperature polymerization of acetylene in an aqueous solution of $\text{CuCl} \cdot \text{NH}_4\text{Cl}$ as a catalyst, with the formation of the primary products of polymerization, *i. e.*, compounds of the aliphatic series, as well as the synthesis of chloroprene rubber, were described for the first time by American chemists.¹ In the work of the American investigators, however, a discontinuous method of polymerization is described, which results substantially in the formation of divinylacetylene and higher polymers of acetylene. Though the American authors consider the formation of monovinylacetylene as an inevitable stage in the polymerization of acetylene, they give no method for its synthesis and simply state that they succeeded in changing the process in such a way that it is possible to obtain monovinylacetylene in good yields. Because of the high complexity of the process, the authors promised to deal with it in a separate article which so far has not appeared.

The investigation described in the present paper was begun in February, 1932, in the Organic Laboratory of GIPKH on the recommendation and with the active co-operation of R. M. Kusk, Director of the Institute. The work was conducted by a group of workers directed by A. L. Klebanskiĭ, L. G. Tzyurikh, I. M. Dolgopol'skiĭ, and Yu. V. Trenke.

Parallel with the research work on synthesis by GIPKH, a study of the use and reworking of the synthetic rubber was conducted by E. D. Kolesov at the Leningrad branch of the NIIRP. In November, 1932, the two Institutes reported to the Government the successful production of a new rubber which was named "Sovprene." Immediately a Government Commission was appointed consisting of the academicians A. E. Favorskiĭ and S. V. Lebedev, the originator of the method of production of synthetic rubber from alcohol, B. V. Buizov, the originator of the method of production of rubber from petroleum, A. A. Yakovkin, Yu. S. Zalkind, and other investigators, under the chairmanship of Svetikov, delegate of the Leningrad People's Committee of Heavy Industry.

The Committee was engaged for an entire month in checking all the details of the process in the laboratory as well as in production on a semi-commercial scale. In its concluding report it recorded several original features of the process developed by the GIPKH, as well as the great advantage of this process compared with other methods of producing synthetic rubber.

Particular attention was called to the high quality of the rubber and its advantage, not only by a comparison with other forms of synthetic rubber, but even with crude rubber with respect to many properties.

Following the decision of the Government Committee and the order of the People's Committee of Heavy Industry, the construction of a large experimental plant for the production of one ton of rubber a day was begun.

The plant was put into operation in July, 1934. It is now operating at full capacity.

Concurrently, the project for the organization of a combine in Erivan, using the power of the Kanakirskiĭ hydroelectric station, was begun.

The technological process of production of Sovprene rubber is carried out in the following stages:

1. A continuous polymerization of acetylene, with the formation of 75-80 per cent of monovinylacetylene as the chief product of the reaction and 20-25 per cent of divinylacetylene and higher polymers as by-products. The utilization of acetylene in the process is 100 per cent.

2. Collection of the products of polymerization and their separation, and the isolation of monovinylacetylene.

3. Addition of hydrogen chloride to monovinylacetylene, with the formation of chloroprene. The resulting increment in weight is practically 50-60 per cent; theoretically 70 per cent.

4. Utilization of the by-products of divinylacetylene and higher polymers by further polymerization to high molecular compounds, which find use as varnish and synthetic driers for oils, either as such or in the form of derivatives. Each stage of the process is treated separately as follows:

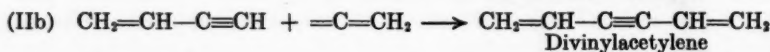
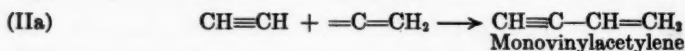
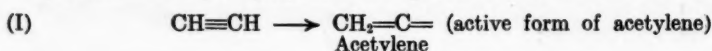
According to the literature already mentioned, the mechanism of the polymerization of acetylene is as follows.

Acetylene in the presence of the complex catalyst, $\text{CuCl} \cdot \text{NH}_4\text{Cl}$, is activated, and changes to the tautomeric acetylide form, thus:

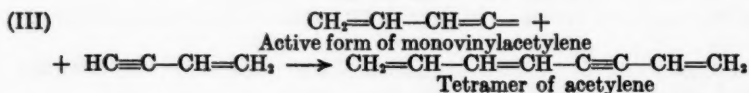
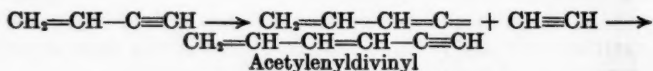


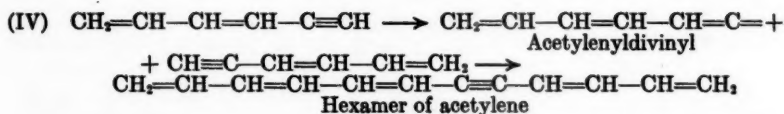
This active acetylene, on entering into the complex compound, reacts with another molecule of acetylene, with the formation of polymerization products. In the first stage a dimer of vinylacetylene is formed, and the latter, as a compound with an active acetylene bond, can itself be activated and combine with another molecule of either acetylene or vinylacetylene. In the first case acetylenyldivinyl is formed, and in the second case vinyldivinylacetylene or tetramer. Monovinylacetylene can also react with a molecule of activated acetylene, with the formation of divinyl acetylene. Acetylenyldivinyl itself, as a compound with an acetylene hydrogen, can also be activated, which, according to Nieuwland, is identical with the conversion to the tautomeric form of the acetylene compound. The resulting active tautomer can react with the inactive molecule of acetylenyldivinyl, with the formation of the hexamer of acetylene (acetylenyldivinyl was not isolated by the American chemists, but was identified for the first time in our laboratory).

The mechanism of the polymerization process is shown in the following scheme:



Monovinylacetylene can also be activated and can then combine with a molecule of acetylene:





The scheme proposed by Nieuwland accords satisfactorily with the composition of the polymerization products obtained, and explains fairly well why precisely these products and not others are formed. According to existing data, though not yet sufficiently demonstrated,² acetylene represents a mixture of two tautomeric forms of inactive acetylene and an active form of the latter, so-called acetylidene, $\text{CH}_2=\text{C}=\text{}$, which is present in ordinary acetylene only in fractions of one per cent. However, in the formation of a complex, the tautomeric equilibrium is evidently shifted toward the active form, because the bivalent carbon is saturated at the cost of the coordinated bonds of the complex.

Thus, because of this shift of equilibrium, it is possible that with the continuous removal of the reaction products the quantity of active acetylene is considerably increased. This increase probably takes place in the solution of the $\text{CuCl}\cdot\text{NH}_4\text{Cl}$ catalyst.

In the process of polymerization a partial decomposition of the original complex takes place, whereby the activated acetylene reacts with the inactivated acetylene molecule. It is possible, however, to explain the mechanism of the reaction of acetylene polymerization without the postulation of such a tautomeric form of acetylene or isoacetylene, the existence of which is not sufficiently demonstrated.

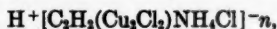
It may be assumed that in the formation of a complex between acetylene and $\text{CuCl}\cdot\text{NH}_4\text{Cl}$, ionization of the acetylene hydrogen³ takes place.

No complexes of acetylene with $\text{CuCl}\cdot\text{NH}_4\text{Cl}$ are described in the literature, though Chavastelon⁴ studied complexes formed by acetylene with cuprous chloride and potassium chloride, and distinguished two forms of the complex:

- (1) $\text{C}_2\text{H}_2[(\text{Cu}_2\text{Cl}_2)\text{KCl}]_2$, yellow
- (2) $\text{C}_2\text{H}_2-(\text{Cu}_2\text{Cl}_2)\text{KCl}$, white

The first complex is formed with insufficient acetylene and the second with an excess of acetylene; the two complexes can change into each other.

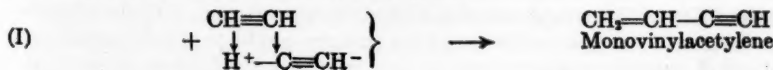
The complex with CuCl and NH_4Cl evidently possesses a much more composite structure: $\text{C}_2\text{H}_2[(\text{Cu}_2\text{Cl}_2)\text{NH}_4\text{Cl}]_3$, and has a golden-orange color, as was established by the present authors. According to the scheme of ionization of acetylene in the complex, the latter formulas may be represented in the following manner:

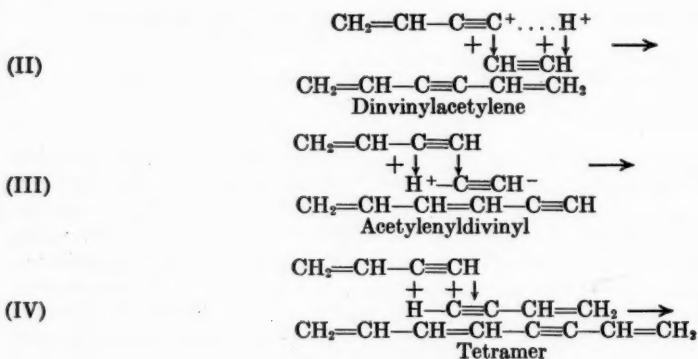


i. e., analogously to our representation of the complex HCl and CuCl as $\text{H}^+(\text{CuCl}_2)^-$ or NH_4Cl and $\text{CuCl} \longrightarrow \text{NH}_4^+(\text{CuCl}_2)^-$.

The question of whether the activated state of acetylene corresponds to the ionized or tautomeric $\text{CH}_2=\text{C}=\text{}$ form of acetylene requires further investigation. This investigation was continued in several ways.

The formation of separate polymerization products of acetylene according to this scheme is represented in the following manner:





As is evident, the difference between this and the previously described scheme is that, in the formation of divinylacetylene, the activation of monovinylacetylene and not that of acetylene is assumed, whereby nothing is substantially changed. An acceptance of such ionization explains the function and the importance of a definite concentration of hydrogen chloride in the catalytic solution. Moreover, this scheme agrees better with the common concept of the structure of complex compounds and the mechanism of such reactions. An analogous scheme is presented in the work of Mignonac et Saint-Annay (*loc. cit.*).

For the development of a method for the synthesis of vinylacetylene suitable for commercial production, the work was carried out in the following manner. At first the method of discontinuous polymerization of acetylene, described by Nieuwland, was investigated, which is as follows.

A highly concentrated solution of CuCl and NH_4Cl in water in the presence of metallic copper is saturated with acetylene, and is allowed to stand 6-7 days at room temperature. The resulting complex is heated, with the distillation of divinylacetylene. During the progress of this investigation it became quite evident that, besides divinylacetylene, it is possible to obtain by this procedure a considerable quantity of monovinylacetylene, in fact more than 10-13 per cent of the acetylene used. By reducing the time of standing of the saturated catalyst to two hours and even less, a yield of 22-25 per cent of monovinylacetylene from the acetylene used was obtained.

Moreover, it was demonstrated that, contrary to Nieuwland, the distillation immediately after saturation results not in the distillation of unchanged acetylene but in that of its products of polymerization, chiefly divinylacetylene. Thus it became obvious that the process of polymerization proceeds at a considerably more rapid rate, and possibly the reaction on contact of acetylene with the catalyst is instantaneous. This observation necessitated a radical change in the method of investigation, based on the fact that the difficulties in the synthesis of monovinylacetylene from acetylene are caused by the further reaction of monovinylacetylene in the presence of a catalyst with a molecule of activated acetylene, with the formation of trimer. In order to eliminate this stage, it was decided to conduct the reaction with immediate distillation of monovinylacetylene after its formation. Proceeding from the conception of the mechanism of the reaction as the formation of a complex of the three components: C_2H_2 , CuCl , and NH_4Cl , the attempt was made to effect the decomposition of this complex at the instant of its formation, with the elimination from the zone of reaction of the resulting primary products of polymerization. This method of immediate removal and cooling results in the fixation of the equi-

librium of the composite system of C_2H_2 , C_4H_4 , and C_6H_6 present in the catalyst in a state of unstable equilibrium. To carry out this idea in practice, the polymerization was conducted in the following manner.

A continuous current of acetylene was conducted at 70–80° C. into the catalyst, which consisted of a concentrated solution of $CuCl$ and NH_4Cl of the following composition: 1000 parts of $CuCl$, 575 parts of NH_4Cl , 1000 parts of water, and 30–35 cc. of HCl (d. 1.19). The catalyst is in a solvated state.⁵

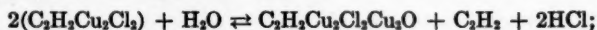
The ratio of mono- and divinylacetylene depends on the duration of contact of acetylene with the catalyst. It is possible to deduce the general rule that the percentage ratio between mono- and divinylacetylene is in inverse ratio to the time of contact. It is possible to obtain a ratio of 90 per cent of monovinylacetylene and 10 per cent of divinylacetylene at corresponding rates of conducted gas, but the percentage of utilization for a single conduction of gas drops to 4–5 per cent. By increasing the contact time, the conversion of acetylene may be increased for a single passage up to 40 per cent and even higher, with an appropriate height of the liquid column, but at the cost of an impaired ratio:

$$\frac{\text{monovinylacetylene}}{\text{divinylacetylene}} \quad (75 : 25)$$

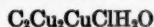
It is evident from the foregoing that at given velocities the degree of conversion of acetylene and the ratio of dimer to trimer depend on the height of the liquid column and the degree of mixing. In order to increase the height of the liquid column and the degree of gas distribution for a greater utilization of acetylene at a given rate, the process is carried out in an apparatus of tower type. The optimum conditions of the process of acetylene polymerization and the influence of various factors were studied in the laboratory and in a pilot plant production. The following factors were carefully investigated: temperature, duration of contact of acetylene with the catalytic medium, the effect of the composition of catalyst, concentration and function of separate components of $CuCl$, NH_4Cl , HCl , and water, and their ratios.

On the basis of a series of experiments it was possible to determine that the maximum activity of the catalyst was at a ratio of the components: $CuCl:NH_4Cl = 1:1$. This ratio, however, can be attained at different concentrations of $CuCl$ and NH_4Cl . By experimenting with various concentrations, it was found that the optimum concentration was within the limits of 30–45 per cent of $CuCl$ contents, the ratio of the components being as shown above.

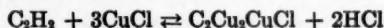
A lower concentration is not practical, because it causes considerable instability of the solution of the complex formed by $CuCl \cdot NH_4Cl$ with C_2H_2 , with its precipitation, and possible hydrolysis, and formation of purple-violet precipitates, according to the following scheme of Chavastelon:



the composition of this complex according to Manchot⁶ is:



Its formation is thus conceived:



According to either of the two schemes, the addition of hydrogen chloride will shift the equilibrium toward the left, with the formation of corresponding complexes. Since the dark violet complex is insoluble and is a product of hydrolytic decomposi-

tion of the active complex CuCl with acetylene, it is evident that its formation is undesirable. Therefore a solution of the catalyst, i. e., a solution of the complex $\text{CuCl} \cdot \text{NH}_4\text{Cl}$ in water, was treated with a little hydrogen chloride (0.5 per cent or less). The addition of hydrogen chloride is necessary not only with a dilute solution of the catalyst, because of the danger of hydrolysis, but also with concentrated solutions in order to obtain a sufficiently effective catalyst. Moreover, it is necessary to add hydrogen chloride to the catalyst constantly, because the latter is continuously consumed by evaporation and as a result of various chemical reactions, produced by conducting acetylene through the catalyst, such as the formation of vinyl chloride, partial oxidation of CuCl to CuCl_2 by atmospheric oxygen, etc.

The function of hydrogen chloride consists possibly in creating a suitable hydrogen-ion concentration required for the formation of the active complex with acetylene.

A marked increase in the concentration of hydrogen chloride results in the formation chiefly of vinyl chloride and acetaldehyde. The optimum temperature interval of the reaction of acetylene polymerization is $50\text{--}100^\circ\text{C}$. Below 50° the solubility of $\text{CuCl} \cdot \text{NH}_4\text{Cl}$ in water is considerably decreased.

Within the given temperature interval, the higher the temperature, the greater is the degree of acetylene conversion for a single passage, and therefore the activity. Moreover, with increasing temperature the ratio of mono- and divinylacetylene also increases.

There is always a danger of resinification by working at lower temperatures, because the higher acetylene polymers are not completely removed from the zone of reaction and are exposed to further polymerization, with the formation of resins. The latter comprise a small percentage (about 0.3–0.4 per cent) of the total amount of the reaction products, but by accumulating in the reaction vessel they cause cementation and clogging, which results in considerable reduction of the reaction activity.

A method of removing the resins by extraction with solvents was developed. The solutions of resins are continuously removed and recovered. Under these conditions the process goes on for a long time without interruption.

The life of the catalyst is very long. The catalyst retained its activity at the end of one to one and one-half months of use in laboratory experiments as well as in large scale production. The operations were interrupted only because of a considerable accumulation of resinous matter in the reacting vessel, since at this stage a method for removing the resins had not been developed.

The problem of construction material for the apparatus is of great importance in commercial production. Since the process is carried on in the presence of hot hydrogen chloride the use of most metals is impossible because of corrosion. It was shown before that the reaction is performed in the presence of copper to reduce any oxidized CuCl catalyst in solution and to prevent oxidation. Since the catalyst is a saturated solution of cuprous chloride, it could be expected that copper would be sufficiently resistant to corrosion. There is no danger of considerable losses of copper by oxidation, because any small amount of catalyst oxidized by atmospheric oxygen contained in acetylene is largely reduced by the acetylene introduced into the solution. In the reduction of cupric chloride formed by oxidation of cuprous chloride in the presence of hydrogen chloride, acetylene is converted into dichloroethane. Proceeding from these observations, copper was selected as the apparatus material. A study of the thermal heat balance of the reaction showed that the required heat can be fully utilized at the cost of the heated gases, and therefore it is possible to use for the construction of equipment any acid-resisting materials, even

poor heat-conducting materials, such as Haveg, fused rocks, etc. The use of wood is not excluded. The advantage of using the latter materials compared with copper is that they eliminate the danger of formation of copper acetylide. Enameled iron apparatus has been used lately with good results.

Collection of Reaction Products

This problem is highly complicated in case of an incomplete and continuous gas reaction. It is made even more difficult by the low boiling point of vinylacetylene (b. p. 5°), the chief product of the reaction, and by a mixture of unchanged acetylene with 20-30 per cent by weight of reaction products. Under these conditions the loss is considerable, requiring cooling of the mixed gases to -70° to -60° for the condensation of vinylacetylene. The difficulties of collection and separation of the reaction products by condensation are intensified to a considerable degree by the detonating properties of some components of the gas mixture. In this respect greater danger is presented by trimers and higher polymers of acetylene capable of forming detonating peroxides in the process of polymerization on contact with air, if no stabilizing agent is added. Because of the difficulties in regulating the condensation at low temperatures, a procedure was developed for the separation of the reaction products and collection of acetylene polymers by the method of selective absorption.⁸ After experimentation with various solvents (xylene, kerosene, solvent naphtha, pyronaphtha, paraffin oil, and their mixtures), xylene was selected as the best solvent of monovinylacetylene which is nearly incapable of dissolving acetylene.

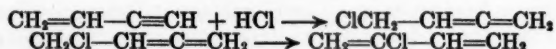
The additional advantage of xylene is that it easily dissolves the polymerization products of acetylene, and in this way aids considerably in their stabilization. The portion of monovinylacetylene retained by xylene after distillation is constant at 0.1 per cent by weight. The optimum temperature of desorption corresponds to the boiling point of xylene, *viz.*, 130-40°.

In the previous gas mixtures it was possible to obtain a concentration of 4-5 per cent of monovinylacetylene in xylene. More recently, because of the increased degree of acetylene conversion at a single passage, reaching 35-40 per cent and higher, the contents of monovinylacetylene in the adsorbent exceeded 10 per cent.

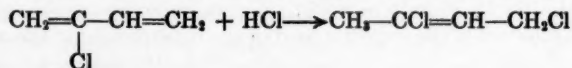
Synthesis of Chloroprene from Monovinylacetylene

(Work performed by K. K. Chevuichalova)

According to Carothers,⁹ the chemical reaction of the production of chloroprene proceeds in the following stages: the first stage is the formation of 4-chloro-1,2-butadiene (b. p. 88°), and the second stage is its isomerization to chloroprene, 2-chloro-1,3-butadiene (b. p. 59.4°). The reaction is represented in the following manner:



In the presence of a large excess of hydrogen chloride, or an excessively long duration of the reaction (over 5 minutes), or at temperatures above 20° C., the reaction proceeds further, with the formation of 2,4-dichloro-2-butene:



The isomerization of 4-chloro-1,2-butadiene to chloroprene proceeds best of all by the action of dilute hydrochloric acid in the presence of the catalyst, $\text{CuCl} \cdot \text{NH}_4\text{Cl}$. In the process of hydrochlorination, the two stages proceed simultaneously without a detention at the intermediate phase. To this end the catalyst $\text{CuCl} \cdot \text{NH}_4\text{Cl}$ is added at once to the solution of hydrochloric acid.

It was established that the first as well as the second stage, *i. e.*, the addition of HCl to monovinylacetylene, with the formation of 4-chloro-1,2-butadiene and the conversion of the latter into chloroprene, takes place in the cold at temperatures of 0° to 5° , *i. e.*, below the boiling point of monovinylacetylene.

This makes it possible to carry out the addition process of hydrogen chloride to monovinylacetylene without pressure. Since chloroprene is capable of a further reaction with hydrogen chloride with the formation of 2,4-dichloro-2-butene, hydrochloric acid containing in solution the catalyst $\text{CuCl} \cdot \text{NH}_4\text{Cl}$ is cooled to 0°C . and introduced into monovinylacetylene cooled to 0°C . The reaction is carried out with energetic stirring because the solutions of catalyst and monovinylacetylene are immiscible liquids. The main portion of the catalyst solution is added at about 5°C ., and the temperature is allowed to rise to 20°C . by the heat liberated in the reaction.¹⁰

The reacted chloroprene is separated from the solution of catalyst, washed free from hydrochloric acid and distilled *in vacuo*, because chloroprene is sensitive to heat and partly polymerizes in the distillation, with the formation of liquid dimers and polymers of poor quality.

The polymerization of chloroprene is decreased by the addition of 0.5–1 per cent of a stabilizing agent, such as pyrogallol, pyrocatechol, Neozone, and other substances. Neozone was used in this work.

In the refining of chloroprene, 10–12 per cent of vat residue of the weight of crude chloroprene is always formed. This residue is composed of dichlorides (25–30 per cent of the residue) and an equal amount of dimers; the balance consists of low-molecular rubber obtained as a result of polymerization at high temperatures and partly decomposed in the distillation of high-boiling dimers. It contains a considerable amount of absorbed terpene dimers, and is therefore quite tacky. The use of these vat residues from the refining of chloroprene will be discussed more fully later.

The spent catalyst solution, containing nearly the entire cuprous chloride and ammonium chloride and a considerable quantity of unreacted hydrogen chloride is regenerated by saturating the solution with gaseous hydrogen chloride and reducing some of the cupric chloride to cuprous chloride. In this operation the content of cuprous chloride is somewhat increased. This excess of cuprous chloride does not affect the reaction of chloroprene production, and it is allowed to accumulate to the danger point of precipitation. When the concentration of cuprous chloride has reached the point of saturation, a part of the solution is freed from copper. The electrochemically treated solution of catalyst is contaminated with traces of organic admixtures, from which it is freed by filtration through activated carbon, or reworked with solvents, such as carbon tetrachloride or tetrachloroethane, and then regenerated by saturation with gaseous hydrogen chloride. The effectiveness of the catalyst is little changed by many repeated regenerations. The same solutions can be used 10 to 15 times or even more. The catalyst is refreshed by gradual additions of the solution freed from the excess copper. In this way the catalyst is completely changed after 15–20 days of work. A very important problem in the process of hydrochlorination is the material used in the construction of the apparatus.

It is well known that no metals or alloys are sufficiently resistant to the action of

concentrated hydrochloric acid. A number of bakelite varnishes were tested for their resistance to the catalyst solution under the conditions of the process of polymerization. As a result of these tests, several grades with fairly good resistance were selected.

Experience of over half a year with experimental production showed satisfactory results with the apparatus protected by this varnish. Lining with ebonite and rubber proved to be impractical, because the protective covering was rapidly destroyed by the action of chloroprene as well as by accelerated aging of rubber caused by the action of the copper salts.

Concurrently, acid-resisting enamel furnished by the Duminicheskii plant was tested, and this proved to be entirely suitable, its durability and length of service greatly exceeding bakelite varnish.

Yu. V. Trenke in the last few years developed in the organic laboratory a method of continuous production of chloroprene from acetylene in one stage without separation of the intermediate product monovinylacetylene. This method of procedure has the following advantages.

1. It simplifies the technical process, eliminating the absorption and desorption of vinylacetylene with a solvent, and makes it possible to conduct the gases after liberation from the higher polymers directly into the reaction chamber where the addition of hydrogen chloride to vinylacetylene takes place. In this way, the polymerization and hydrochlorination of acetylene proceed in one stage.

2. The process of hydrochlorination is also greatly simplified in respect to the mechanical construction of apparatus by substituting tower type units for the apparatus with stirring devices. The former are more easily constructed from any acid-resistant material, which is not an unimportant factor when the difficulties of working with hydrochloric acid are considered.

3. The great advantage of this method is that the continuous procedure of this part of the process results in a considerable increase in the productivity of the apparatus.

4. Because of the presence of a large excess of free gas, no effective cooling is required, which is very important, considering the rigorous temperature regulation required in the reaction of hydrochlorination of vinylacetylene in order to avoid the formation of dichlorides. The difficulties of producing chloroprene in the presence of acetylene are caused by the ability of acetylene to add hydrogen chloride by the action of catalysts in hydrochloric acid solution. As a result of a systematic study of the behavior of the separate components of the gas mixture (acetylene and monovinylacetylene) under different conditions of concentration of hydrochloric acid and cuprous chloride and various periods of contact, it was possible to determine the exact conditions under which the addition of hydrogen chloride to acetylene with the formation of vinyl chloride is practically eliminated. The addition reaction of hydrogen chloride to vinylacetylene proceeds in a gaseous phase very actively even on short contact, which renders the continuous process possible. Under definite conditions of optimum procedure (concentrations of HCl about 25-7 per cent and of catalyst 10-12 per cent of CuCl, and temperature 20° C.), the addition of hydrogen chloride to vinylacetylene only, and none to acetylene, takes place. The yield of chloroprene under these conditions reaches 80 per cent and higher.

The necessary condition to the successful performance of the entire reaction by a continuous procedure is the liberation of the gaseous mixture from divinylacetylene. The latter may be substantially separated by condensation at -25° C. with a solution of calcium chloride, and partial absorption by xylene. The remaining small residue can be removed by careful distillation, since the difference between

the boiling points of chloroprene and divinylacetylene is 23–24° C. at 760 mm. pressure.

Studies of the active life of the catalyst showed that under the conditions prevailing in the continuous process it retains its activity for a considerable time without regeneration. The productivity is fifty-fold quantity by weight of chloroprene to 1 g. of cuprous chloride. After this the catalyst may be regenerated.

Polymerization of Chloroprene

(Work performed by E. Z. Margules and R. M. Sorokina)

Though the process of polymerization of chloroprene is described in the literature,¹¹ it is so complicated and its mechanism is so little explained that it was necessary to make a detailed study of it, since the quality of rubber depends chiefly on the conditions of polymerization. The polymerization is highly complicated by the formation of various polymers. Thus Carothers (*loc. cit.*) has identified five separate modifications, which differ sharply in their physical properties (solubility, consistency) and influence the quality of the rubber. These polymers are α -polymer, μ -polymer, balata-like polymer, ω -polymer, and liquid dimers.

All these polymers are not individual compounds, and a technical polymer is, undoubtedly, a complex mixture of separate modifications in various proportions. The correlation of these separate components determines the method of technical reworking as well as the properties of the resulting rubber.

Of special technical interest are the two polymers, α -polymer and μ -polymer. The α -polymer is a soft, plastic substance, which gives on thermal vulcanization an elastic, durable rubber. It is therefore used as synthetic rubber. α -Polymer is characterized by considerable instability, undergoing a further spontaneous polymerization on storage with conversion to the μ -polymer, which resembles vulcanized rubber and is less suitable to further reworking. This transition from the α - to the μ -modification begins at a definite stage of polymerization, whereby this conversion proceeds much more rapidly than the formation of the α -polymer. These circumstances make it obvious that it is impracticable to conduct the polymerization to the end, and that it must be stopped at a definite stage corresponding to the α -polymer.

The results of a long series of experiments indicate that the optimum limit is 30–35 per cent polymerization. At this stage the polymerization must be discontinued, and on the addition of a stabilizing agent (about 2 per cent of Neozone), the unchanged chloroprene is distilled off, preferably *in vacuo*, with stirring in the Werner-Pfleiderer apparatus.

Spontaneous polymerization proceeds quite slowly; in fact four days at 20–5° C. are necessary to bring it to the required limit. By elevating the temperature to 30–35° C., polymerization can be somewhat accelerated and the elapsed time can be reduced to 2–3 days. A further increase of the temperature increases considerably the rate of polymerization, but results in a rubber of poor quality. Thus rubber obtained from chloroprene polymerized at 45° C. and higher has a tensile strength of 50–60 kg. per sq. cm., compared with a product polymerized at 25–30° C., which has a tensile strength of 250–300 kg. per sq. cm. This shows conclusively that the method of forced polymerization at elevated temperature is not rational, since it leads to a disproportionate impairment of the quality of polymer. The optimum temperature of 30–5° C., with 20–5 per cent polymerization in three days, was accepted as a standard for practical production. The polymerization is greatly accelerated by the addition of water or a dilute aqueous solution of an alkali or ammonia. This method of polymerization was worked out from every angle. Not-

withstanding the advantages of considerable acceleration on the addition of water, the process was not adapted to a large scale production, because it is difficult to control and proceeds frequently at a certain stage of the polymerization by an uncontrollably violent reaction, with liberation of considerable heat and conversion of the polymer to the μ -modification.

Attempts to accelerate the polymerization by addition of catalysts in the form of peroxide compounds (benzoyl peroxide and other compounds in various concentrations) produced no desired results. It must be noted that the slower the process of polymerization, the better is the quality of the rubber.

A polymer of highest quality, with a tensile strength of 300–50 kg. per cm., at a relative elongation of 850–1000 per cent at the breaking point, is obtained by polymerization in a nitrogen atmosphere at 20–5° C. for 5–6 days. Irradiation has a positive effect on the velocity of polymerization, the active principle being the violet part of the spectrum, such as is obtained from a mercury glass lamp. The polymerization is performed in a glass apparatus. Under these conditions a 30 per cent polymerization at 30–35° C. is effected in 36–48 hours instead of 3–5 days at room temperature in diffused light. The mercury arc can be replaced by an electric incandescent lamp of 500–1000 watts.

Filippov and Talmachev studied in the State Optical Institute the problems related to the effect of light on the polymerization. The experimental results lead to the following conclusions:

1. The absorption of light by chloroprene begins at the visible part of the spectrum, though very faintly. Absorption gradually increases toward the short wave lengths. The entire light of 3000 to 2250 A. U. is completely absorbed by a layer of 1 cm. At a thickness of 8 cm. a similar absorption is observed. Complete absorption begins at 3350 A. U.

2. At 45 per cent polymerization of chloroprene, the product shows a considerably increased absorption in the blue part of the spectrum. A complete absorption for 1 cm. layer begins at 3750 A. U.

3. Chloroprene vapors of 1 cm. thickness completely absorb light of the wave length of 2570–2580 A. U.

4. A selection of the sources of light is determined according to the data on absorption and the action of light. A very suitable source of light for the acceleration of the polymerization of chloroprene is an iron arc with direct current, which gives a powerful emission of radiation throughout the ultra-violet and the short visible ranges. In place of an iron arc can be recommended an arc of carbon electrodes containing up to 50 per cent of ferric oxide, or a carbon arc with admixtures of rare earths and thorium. The use of a quartz mercury arc is not advisable, because radiation of shorter wave lengths than 2000 A. U. promote the formation of ω -polymer.

A mercury arc in Uviol glass, transmitting light to 3000 A. U., is most suitable. Finally, common incandescent lamps can be used, but because of the weak action of the visible light, lamps of very high power are required.

The stabilization of rubber is a problem of great importance. The process of polymerization in the absence of a stabilizing agent proceeds beyond the stage of α -polymer, with formation of products of further polymerization and oxidation accompanied by discoloration and partial decomposition of rubber, with liberation of hydrogen chloride. Stabilization eliminates these processes. A stabilizing agent retards the aging of rubber, but does not prevent hardening.

This hardening is only superficial, and disappears after reworking on a mill with heating, the rubber recovering its original elasticity and softness.

Hardening of the rubber is a great detriment, but by changing the conditions of

polymerization it was successfully overcome. A large number of samples of chloroprene rubber produced in the laboratory and pilot plant after one year of storage fully retained their softness, without any signs of hardening.

The essential changes made consist of polymerization in the absence of oxygen, *i. e.*, in an atmosphere of nitrogen or carbon dioxide.

The processes of aging and hardening of rubber are related to the many polymer forms.

It is well known that besides the α - and μ -polymers there are granular, insoluble ω -polymer and balata-like products, which are solid at room temperature and soft and tacky when hot. An ordinary sample of polymer rarely consists of an individual polymer, but usually the products are mixtures, with some modification predominating. Since separate forms of polymer are capable of catalyzing their formation, there is a possibility of a mutual conversion. Because of the irreversibility of the process, it is probable that α -polymer, having a relatively more simple structure, will be irreversibly transformed into a more complex compound with higher molecular weight, such as μ -polymer or balata-like polymer.

Because of this catalytic action of polymers, it is important to exclude them in the initial stages of polymerization. The results of extensive experimentation showed that chloroprene rubber is highly sensitive to the action of atmospheric oxygen. Thus the soft rubber, stabilized with Neozone, on exposure to air is gradually converted into a balata-like product. This is characteristic of the samples obtained on metallic surfaces. This transformation may be ascribed to the action of atmospheric oxygen. It was in fact observed that in most cases rubber hardens on the surface, and changes to the balata form. The smaller the samples, and the greater the corresponding surface, the deeper does the hardening penetrate. It may be assumed that hardening is caused by the formation of balata-like polymers and subsequent transformation of the entire rubber under the action of oxygen.

The effect of atmospheric oxygen was studied by comparative tests on the polymerization of chloroprene in atmospheric oxygen and various inert gases, such as nitrogen and carbon dioxide.

It should be noted that polymerization in an inert gas proceeds more slowly, giving polymers of entirely different character. Even a casual observation showed that the product obtained by polymerization in an inert gas or in a medium with insufficient influx of air by working in hermetically sealed apparatus, is much more viscous than are the corresponding products with the same contents of polymers obtained by polymerization with large quantities of air. Therefore the physical constants (coefficients of refraction, relative and specific viscosities and densities) of 5 per cent solutions of polymerized products of different degrees of polymerization were studied in relation to the influence of the gaseous environment.

The changes of the physical properties were studied with three samples obtained in atmospheres of nitrogen, carbon dioxide, and air¹² (Figs. 1 and 2).

The graphs show that the curve of increasing viscosity of the samples polymerized in air is very oblique, and at 44 per cent polymerization, *i. e.*, at 2.2 per cent concentration of the polymer in solution, is 1.7. For a sample polymerized in nitrogen and at the same concentration of the polymer, the viscosity is 17, or ten times greater than that of the sample polymerized in air and tested at the same concentration. Obviously the character of a polymer obtained in an inert gas is essentially different from one polymerized in air. The results obtained in nitrogen and carbon dioxide are analogous. The graphs also show the difference in the densities. The density of polymerized chloroprene with equal polymer contents is greater for the products polymerized in nitrogen and lower for those polymerized in air. Moreover the samples polymerized in nitrogen do not harden. The process

presents considerable difficulty because of the necessity of carrying out the polymerization only partially (25–30 per cent) and distilling off the unchanged chloroprene.

A method was developed for complete polymerization, with the production of α -polymer, without an intermediate distillation and separation of the polymerization product. This was made possible by polymerization in solvents. We proceeded from the following idea.

α -Polymer is, in our conception, a thread-like linear polymer. Its conversion into the μ -polymer involves combining the separate linear chains into a crystalline network. The velocity of this union of separate linear chains is evidently a function of the concentration. It can be assumed that at low concentrations the unchanged chloroprene acts as a solvent, forming a solvate shell around the polymer

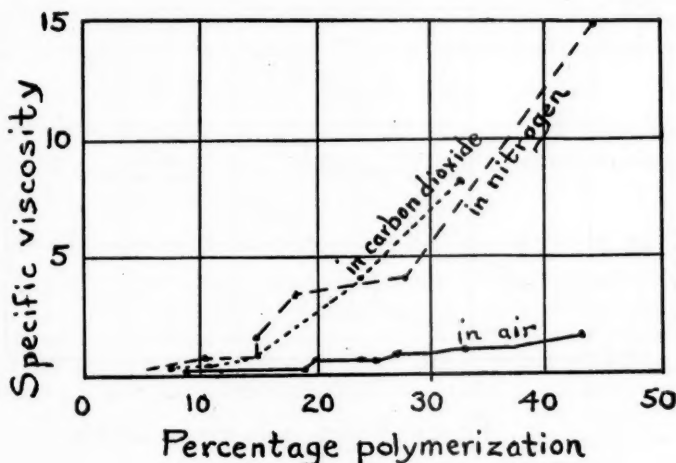


Figure 1

chains, thereby protecting them from the formation of spatial structures which are formed by the mutual interaction of separate chains.

Under the usual conditions of polymerization, chloroprene itself acts as such a diluent. Since the molecules of solvate shell in the presence of chloroprene are themselves capable of activation, it follows that at a definite concentration of polymer they begin to unite with each other, thus forming a network. By substituting inert diluents for chloroprene, it is possible to achieve 100 per cent polymerization, with the formation of pure α -polymer, *i. e.*, a product composed of separate linear chains not united with each other. There is no necessity to dilute the mixture at the very start, because at the initial stages of the concentration of polymer of 20 per cent there is no danger of forming α -polymer, since chloroprene acts as a solvent.

Thus the duration of polymerization is reduced at the first stage to three days at room temperature (20–25° C.) and to 30–36 hours by the use of irradiation and a temperature of 30–35° C. Beginning with a concentration of 20–25 per cent of polymer, the solvent is gradually added in order to maintain the concentration at the same point.

To increase the velocity of polymerization at this stage, the temperature is raised to 60° C., which does not affect the quality of the resulting rubber.

By this procedure, polymerization is effected in only 5-8 days and gives exclusively α -polymer.¹³ The latter can be separated either by vacuum distillation of the solvent or by precipitation with alcohol.

This simplified process of polymerization results in a soft plastic product, which shows no tendency to harden. The process of polymerization under these conditions is evidently less sensitive to various catalytic actions, and therefore the problem of selection of suitable material for the apparatus is considerably simplified.¹⁴

It must be said that the problem of material for the construction of the apparatus presents many difficulties because of the sensitiveness of the process to catalytic influences. On the basis of a series of experiments with various metals, it was ascertained that all metals except nickel, silver, gold, and platinum exert a detrimental influence on the quality of rubber. All of them cause the formation of ω - and balata-

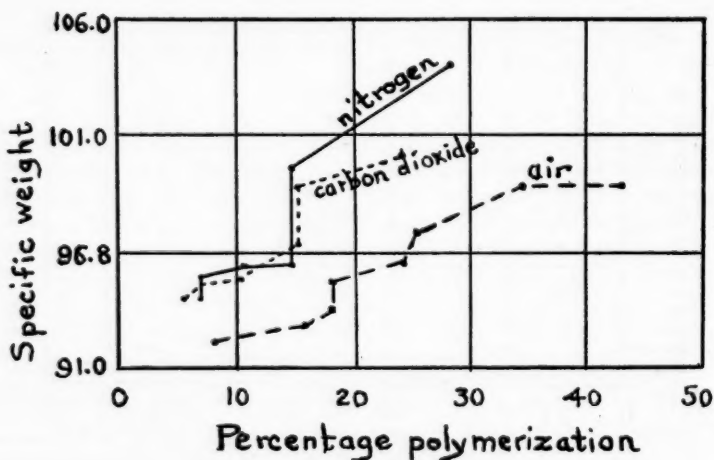


Figure 2

like polymers. This action of metals is evidently caused by the formation of lower chlorides of metals at the cost of the gaseous hydrogen chloride liberated in small amounts during the polymerization. In fact, the addition of metallic chlorides to chloroprene causes the formation of ω -polymer. This explains why the noble metals do not influence the reaction. The quality of polymers obtained in the presence of metals is very poor. The rubber polymerized in the presence of metals frequently tends to age poorly. The suitability of nickel requires further study.

The best material for the polymerization of chloroprene into rubber is an apparatus lined with acid-resisting enamel of bakelite of stage C. Very suitable materials are certain grades of cement, which, because they are porous, can be impregnated with bakelite varnish.

Mechanism of Polymerization of Chloroprene and the Structure of Polymers

(Work performed by V. G. Vasil'eva and others)

Besides the study of the technology of the polymerization of chloroprene, considerable work was carried out in investigating the mechanism of polymerization and the conditions of the formation of separate polymers and their structure.

The Staudinger method was used in a study of the size of the molecules of polymers in relation to the conditions of polymerization and various other factors.

The determination of the molecular weights by the method of isothermic distillation of Barger, Signer, and other investigators is now being studied.

Composition of Higher Polymers of Acetylene

(Work performed by I. M. Dobromil'skaya and U. A. Dranitzuina)

It was shown above that in the polymerization of acetylene there is formed, besides monovinylacetylene, about 25 per cent of higher polymers, containing about 80 per cent of divinylacetylene and 20 per cent of tetramer. Together with the already known higher polymers of acetylene, *i. e.*, divinylacetylene and tetramer, considerable quantities of new compounds were discovered in the products of the acetylene polymerization: *acetylenyldivinyl*, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{C}\equiv\text{CH}$, and an *isomer of tetramer*, which, we believe, has the structure of *acetylenylhexatriene*, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}\equiv\text{CH}$.

These compounds indicate the possibility of a considerable degree of activation, not only of acetylene but also of monovinylacetylene and acetylenyldivinyl, in the process of polymerization.

The structure of acetylenyldivinyl was determined and its properties were investigated. It is a liquid, boiling 30–32° C. at 100 mm., and d_{20}^{20} 0.7821 and n_D^{20} 1.49. With methylmagnesium iodide it gives methane, which shows the presence of acetylene hydrogen. It forms copper derivatives of light yellow and silver-white colors. The copper derivatives were obtained by treating acetylenyldivinyl with Illosvey solution. The product, obtained in nearly theoretical yield, was dried *in vacuo* to a constant weight and analyzed, giving 45.19 per cent of Cu; calculated for $\text{C}_6\text{H}_5\text{Cu}$ 45.23 per cent Cu. Acetylenyldivinyl is easily discolored to yellow in air, is unusually rapidly oxidized, and to a considerable degree accelerates the formation of explosive peroxide compounds. Pure divinylacetylene is more stable to the action of atmospheric oxygen, and it oxidizes more slowly than does acetylenyldivinyl. By the addition of hydrogen chloride to acetylenyldivinyl it was possible to obtain a compound, to which by analogy with monovinylacetylene is ascribed the structure of *vinylchloroprene*:



a liquid, boiling at 40–41° at 25 mm., d_{20}^{20} 0.9639, n_D^{20} 1.519. It polymerizes in air with extraordinary speed. The properties of its polymers are being investigated.

A technically suitable procedure for the separation of acetylenyldivinyl and divinylacetylene from the mixture of polymerization products is being investigated. As was said before, it was possible to identify also an isomer of the tetramer among the higher polymers of acetylene. This isomer is a liquid, boiling at 44° C. at 20 mm. pressure, 51° C. at 30 mm.; d_{20}^{20} 0.857; n_D^{20} 1.489.

Polymerization of the Higher Fractions of Acetylene Hydrocarbons (Trimer, Tetramer, and Other Polymers)

(Work performed by Levina and Krasinskaya)

For the utilization of the higher polymers of acetylene, they were subjected to further polymerization. Considerable work was carried out in investigating the conditions of polymerization of monovinylacetylene, divinylacetylene, acetylenyldivinyl, the tetramer of acetylene and their mixtures in various proportions. The conditions of polymerization were studied in relation to the temperature, with and

without the use of various solvents. The rates of polymerization in relation to the temperature and concentration, the effect of various stabilizing agents of various concentrations on the velocity of the process, and the property of the polymers, were investigated. As the result of this work, the optimum conditions of polymerization of separate polymers were developed, and graphs of the coefficients of refraction, density, and viscosity in relation to the degree of polymerization and other factors were made.

The following relations were established:

1. Of all the polymers of acetylene, acetylenyldivinyl is polymerized most rapidly. Divinylacetylene freed from acetylenyldivinyl polymerizes considerably more slowly. The polymerization of the tetramer is still slower, but more rapid than that of monovinylacetylene.

2. The polymerization of all the components is greatly accelerated by the presence of small admixtures of oxygen, but there is a danger of the formation of detonating peroxidic compounds. In the presence of a stabilizing agent up to 0.1 per cent, the formation of peroxidic compounds is eliminated. A study was made of the rate of oxidation of separate polymers of acetylene in pure oxygen and air, with and without the addition of various stabilizing agents in various proportions. The influence of solvents, irradiation, moisture, and factors was also investigated.

It was found that in the presence of 0.1 per cent of a stabilizing agent no absorption of oxygen takes place. Oxidation is also retarded by the presence of solvents. Explosions are caused by peroxides in a solid state. Soluble peroxides are not explosive. On heating with water, the peroxides decompose, with the formation of aldehydes, acids, and other decomposition products.

The presence of peroxides was determined by their reactions with titanium chloride, ferrous salts in the presence of ammonium thiocyanate, and by other methods.

Polymers obtained in an atmosphere of inert gases are not explosive if polymerization is carried out to the end, and the initial product is not exposed to the action of oxygen (*i. e.*, if it is distilled and stored in an inert gas).

On the basis of the investigation of the properties of polymerized trimers and tetramers, the following method for their polymerization into varnishes and drying agents was developed. A 25–50 per cent solution of polymer in xylene or some other solvent, with 0.3–1 per cent of hydroquinone as stabilizer, is heated in an inert gas for 50–60 hours. To obtain soluble polymers, the polymerization is carried out to 60–70 per cent, otherwise gelatinization with a subsequent formation of solid and completely insoluble polymers takes place.

The unpolymerized mixture of hydrocarbons (mostly trimers) is distilled off in a mixture with xylene and is used again in the polymerization.

The resulting solution of polymers is a varnish. The product tested as painters' varnish showed great durability, hardness, and good luster. It dries at 50° in a thermostat in 15–30 min. and in air in 12–15 hours. It is resistant to the action of fuming hydrochloric acid, nitric acid, 50 per cent sulfuric acid and alkalis. The duration of the tests was about 5 months.

Hydrochlorination and Chlorination of Trimers of Acetylene and Their Polymers

On the basis of their structure and the determination of the iodine number, the polymers of acetylene hydrocarbons are highly unsaturated compounds with double and triple bonds; hence there is ground for the belief that this unsaturated condition is the cause of quick drying of the polymers with the formation of higher degrees of polymerization, probably of spatial structure. This state is evidently reached when

the polymer is freed from the solvent, since in solution a polymer contains linear chains. A possibility of inclusion of cyclic compounds (cyclobutane) in the chain is not excluded, as this was demonstrated by Carothers.¹⁵ This advanced polymerization evidently is the cause of some brittleness of the lacquers when applied to metals.

For the purpose of changing these properties of the polymers, it was considered necessary to decrease their degree of unsaturation.

To this end a series of derivatives of acetylene trimers was produced, *viz.*, addition products of chlorine and hydrogen chloride of various degrees of chlorination and hydrochlorination, whereby the reactions were carried out with the initial hydrocarbons and their polymers. The resulting halogenated polymers gave a considerably more elastic film. To reduce the unsaturated degree of the initial products and their polymers, they were hydrogenated, *i. e.*, etherized and esterified by the addition of various alcohols and organic acids at the unsaturated bonds, as well as hydrated to obtain the corresponding ketones.

Utilization of Waste Products of Hydrochlorination of Monovinylacetylene

Besides the products formed in the polymerization of acetylene, which have been mentioned already, the synthesis of chloroprene results in the formation of about 15 per cent of waste products, based on the weight of chloroprene obtained.

These waste products are composed of: (1) dichlorides, including 2,4-dichloro-2-butene, formed by the addition of a second molecule of HCl to chloroprene, $\text{CH}_2\text{Cl}-\text{CH}=\text{CCl}-\text{CH}_3$, in 35 per cent of the total quantity of waste products; (2) a mixture of dimers formed as the result of polymerization of chloroprene in the presence of a stabilizing agent at high temperatures, and having the structure of cyclic terpenes, and (3) an unreacted fraction of lower polymers of chloroprene rubber, formed by the thermal polymerization of chloroprene, and probably different from the usual chloroprene polymer by a considerably smaller molecular weight.

The third fraction remains in the residue of the vacuum distillation of dichlorides and dimers.

The last two fractions (dimers and undistilled residue) are capable of forming films, and are added as plasticizers to lacquers in proportions of 30 per cent and over, based on the weight of pure polymer. Because of the good elasticity of the films formed by these fractions, they function not simply as loading agents but as agents which improve the qualities of varnish.

The utilization of dichlorides presents considerably greater difficulties.

Attempts to obtain chloroprene from dichlorides by removal of HCl with alcoholic alkalis resulted only in the formation of the simple *chlorobutanol ethyl ether*, $\text{CH}_3\text{CCl}:\text{CHCH}_2\text{OC}_2\text{H}_5$, b. p., 143°C ., $62-4^\circ\text{C}$. at 40 mm.; d_{20}^{20} 0.9729; n_D^{20} 1.4382; molecular weight (cryoscopic in benzene) 137.8, calculated for $\text{C}_6\text{H}_{12}\text{ClO}$, 134.6.

Analysis	Found %	Calculated %
Cl (Carius)	26.7	26.39
C (Libig)	54.04	53.6
H (Libig)	8.01	8.17
O (by difference)	11.78	11.88

Attempts to substitute this product for amyl acetate in the lacquer and plastics industry have not been satisfactory. The dichloride on saponification gave *2-chloro-2-butene-4-ol*, $\text{CH}_3\text{CCl}:\text{CHCH}_2\text{OH}$, b. p. 92°C . at 50 mm. pressure; d_{20}^{20} 1.106; molecular weight (cryoscopic in nitrobenzene) 116.5 (found), 106.5 (calcd.)

Analysis	Found %	Calculated %
Cl	32.8	33.3
C	45.33	45.07
H	6.47	6.57
O	15.4	15.06

This alcohol treated with carbon sulfide in alkaline solution gave the corresponding xanthate, which as a flotation agent is equal to American ethyl xanthate. An equimolecular mixture of the alcohol and dichloride heated with an aqueous solution of alkali gives a simple *dichlorobutenyl ether*, $\text{CH}_3\text{CCl}=\text{CHCH}_2\text{OCH}_2\text{CH}:\text{CClCH}_3$, b. p. 142°C . at 50 mm.; d_{20}^{20} 1.1171; n_D^{20} 1.486; MR 50.11 (observed), 49.16 (calculated); molecular weight (cryoscopic in benzene) 194.15 (observed), 194.2 (calculated)

Analysis	Found %	Calculated %
Cl	36.26	36.41
C	50.26	49.25
H	6.26	6.2

The waste products of the chloroprene synthesis can also be utilized in other ways. By condensation of the separate fractions of residues and the entire mixture with alkali polysulfides, a series of polymer compounds of high molecular weight, *i. e.*, *thio-rubbers*, was obtained. These compounds differ greatly in their solubilities and other properties, and can find application, depending on the degree of polymerization, as softeners for rubber or varnishes.¹⁶

New Derivatives of Acetylene Polymers

Because of the unusually high reactivity of monovinylacetylene, it should find a very wide application in the synthesis of a great number of new derivatives of the butadiene series. Since the hydrocarbons of this series are easily polymerized, with the formation of rubber-like polymers, an unusually far-reaching possibility presents itself for the synthesis of several series of new compounds and new rubbers, which may be expected to possess the most varied properties. Accordingly there are possible ways of synthesizing various types of rubber for use in different fields of industry. Of the different products synthesized the following are worthy of note:

1. α,β -Dichlorobutadiene and its polymerization products.
2. Ethoxy-1,3-butadiene and 1-methoxy-3,4-butadiene.
3. Styrene by polymerization of monovinylacetylene.
4. Formoprene (2-formoxy-1,3-butadiene) and acetoprene (2-acetoxy-1,3-butadiene).
5. Hydrogenation of monovinylacetylene to butadiene. Because of space limitations, the nature and properties of these products are only reviewed briefly here.

Synthesis of α,β -Dichlorobutadiene¹⁷

(Work performed by A. S. Vol'kenshtein and A. P. Orlova)

Chlorine at the double bonds strongly activates the molecule of an organic compound, increasing its ability to polymerize. Thus propylene is polymerized only at very high temperatures and considerable pressure, while vinyl chloride is polymerized comparatively easily. The rate of polymerization of chloroprene, according to Carothers, is 700 times greater than that of isoprene. The velocity of spontaneous polymerization of dichlorobutadiene is 7000 times greater than that of isoprene.¹⁸ To determine the influence of chlorine on the polymerization of compounds with

double and triple bonds, 1,2-dichloro-1,3-butadiene was synthesized in the following manner. Monovinylacetylene treated with sodium hypochlorite gave 1-chloro-2-vinylacetylene. This when treated with supersaturated hydrochloric acid (obtained by saturating concentrated hydrochloric acid with gaseous hydrogen chloride at 0° C.) in the presence of $\text{CuCl} \cdot \text{NH}_4\text{Cl}$ as catalyst gave 1,2-dichloro-1,3-butadiene. These two products were synthesized for the first time in this laboratory with 60–70 per cent yields. 1-Chloro-2-vinylacetylene is a liquid, boiling at 55–7° C. under 760 mm. pressure; d_4^{25} 1.021; n_D^{25} 1.4698; MR 23.51 (observed), MR 22.97 (calculated); Cl 41.33 per cent (determined), 41 per cent (calculated).¹⁹

Contrary to Carothers, this compound is not explosive and, when stabilized with hydroquinone, can be distilled under atmospheric pressure. The high explosiveness, observed by Carothers, is caused by the presence of acetylene in monovinylacetylene, which leads to the formation of highly explosive dichloroacetylidene or the polymers explosive in the absence of stabilizers.

The presence of chlorine at the triple bond greatly accelerates polymerization, compared with monovinylacetylene. 1,2-Dichloro-1,3-butadiene is a liquid, boiling at 60–65° C. at 40 mm. pressure; d_{15}^{15} 1.207; n_D^{15} 1.5078; MR 30.47 (observed), 29.47 (calculated); exaltation 0.998; Cl 58.07 per cent (determined), 57.68 per cent (calculated). It polymerizes much more slowly than chloroprene (70 per cent polymerization at 50° C. in 5 days). Evidently the presence of a halogen in α -position retards polymerization. The product when completely polymerized is soluble in chloroform and benzene, and therefore is α -polymer. It follows that a second halogen in the 1-position retards the polymerization of α -polymer and its conversion into μ -polymer. The polymer of dichlorobutadiene on vulcanization gives a product with properties resembling ebonite. Thus, introduction of an additional atom of chlorine causes great changes in the properties of a polymer.

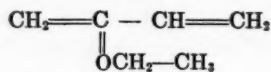
Synthesis of Ethoxy- and Methoxybutadiene

(Work performed by I. A. Rotenberg and M. A. Favorskii)

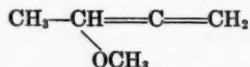
Besides the halogen derivatives of butadiene, it was of interest to investigate butadiene ethers with a view to synthesizing new forms of rubber.

Monovinylacetylene, capable of reacting with alcohols and acids, is of special interest as a starting material. The reaction was carried out by the method of Favorskii, i. e., by heating monovinylacetylene with alcoholic alkalies at 150° C. for 10–18 hours. It was found that ethyl alcohol and methyl alcohol react differently.

With ethyl alcohol, *2-ethoxy-1,3-butadiene* is formed:

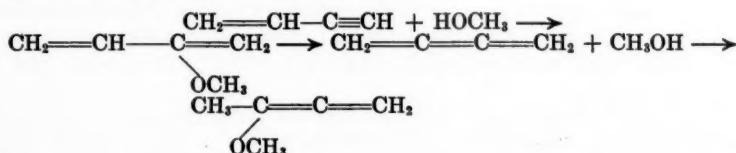


With methyl alcohol *2-methoxy-3,4-butadiene* is formed:



The formation of this compound under the particular conditions is best explained by the scheme proposed by Favorskii for interpreting the mechanism of isomerization of acetylene hydrocarbons.²⁰ At first, the addition of the particles of methyl alcohol to monovinylacetylene takes place with the formation of 2-methoxybuta-

diene, followed by the cleavage of methyl alcohol and secondary addition in the 1,2-position, according to the following equation:



This formula agrees with the degradation products obtained by oxidation with potassium permanganate and hydration with dilute sulfuric acid. In fact, the oxidation with permanganate in alkaline solution results in the formation of a single product of acetic acid, identified as silver acetate. The ozonization gives only formic acid; no oxalic acid in the products of ozonization could be detected. No traces of methoxyacetic acid could be found.

The hydration with dilute sulfuric acid in the presence of mercuric oxide as catalyst gives methylvinyl ketone.

The addition product of methyl alcohol and monovinylacetylene boils at 97° C., 33° C. at 27 mm. pressure; d_4^{20} 0.8497; n_D^{20} 1.437; MR 25.98 (observed), 25.94 (calculated); molecular weight (cryoscopic in benzene) 83.9 (determined), 84 (calculated).

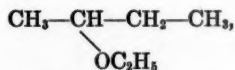
In the formation of 2-ethoxy-1,3-butadiene from ethyl alcohol and monovinylacetylene, the addition reaction stops at the first stage of the scheme above. The nature of the addition products is governed by the velocity of the separate stages of the reaction; and it is possible that in the case of the ethoxy derivative the second stage proceeds more slowly. This product has the following constants:

Boiling point 113.4° C.; d_4^{20} 0.839; n_D^{20} 1.43

Molecular Weight	Observed	Calculated
Cryoscopic in benzene	97.3	98
Ethoxy number (Zeissel)	0.06	0.062
Carbon	73.89%	73.47%
Hydrogen	10.33%	10.26%
Oxygen (by difference)	15.88%	16.33%

The structure of this compound was determined in the following manner.

The presence of a conjugated system of double bonds was disclosed by oxidation with potassium permanganate and ozonization; the decomposition products are oxalic and formic acids. The position of the ethoxy group was demonstrated by hydrogenation; the resulting product is the ethyl ether of secondary butyl alcohol of the following structure:



which shows that the product is β -ethoxy-1,3-butadiene. The constants of the hydrogenation product are as follows:

Boiling point 79–80° C. at 760 mm.; d_4^{20} 0.6363; n_D^{20} 1.378

According to the literature (*Compt. rend.*, 2, 354 (1932)) $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)\text{CH}_2\text{CH}_3$ boils at 81.2° C., d_4^{25} 0.7377, n_D^{25} 1.3755. The boiling point of the ethyl ether of primary butyl alcohol is 92.3° C., d_4^{25} 0.7447, n_D^{25} 1.3798 (cf. *J. Am. Chem. Soc.*, 54, 2088–100). Moreover hydration with dilute sulfuric acid in the presence of mer-

cury salts gave methylvinyl ketone, which also proves that the ethoxy group is in β -position. On heating monovinylacetylene with methyl alcohol in an autoclave at 150° C. for 18 hours, a fairly large yield of a product was obtained, which boiled at 39° C. at 9 mm.; molecular weight (cryoscopic in benzene) 100, theoretical 104 for C_5H_8 ; n_D^{20} 1.528; d_{20}^{20} 0.9139; MR 35.02 (observed), MR 34.972 calculated for styrene.

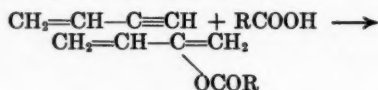
According to the constants and the resulting dibromide the product is styrene. The dibromide, recrystallized from alcohol, melts at 72° C.; when mixed with pure dibromostyrene it gives no depression of the melting point.²¹ It is interesting to note that Carothers,²² on heating monovinylacetylene with sodium alcoholates at 100–5° C., obtained as the only product, not the corresponding diene ether, but the 1-alkoxy-2,3-butene $\text{RO}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_3$.

The syntheses of the ethoxy- and methoxy derivatives of butadiene were also effected in the presence of mercuric oxide and boron trifluoride catalysts. The reaction in methyl alcohol was performed with either boron trifluoride or its complex $(C_2H_5)_2O.BF_3$. A study of the structure of the products of synthesis is being continued.

Addition of Organic Acids to Monovinylacetylene

(Work performed by K. K. Chevuichalova)

Besides the derivatives of alcohols, it was of interest to investigate the composite esters of butadiene obtained from monovinylacetylene and organic acids. These esters are obtained according to the general scheme:



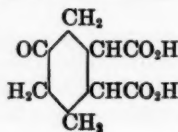
The reaction is carried out by conducting monovinylacetylene into a corresponding organic acid in the presence of mercuric sulfate as catalyst at room temperature. The same reaction proceeds with better yields in the presence of the catalysts mercuric oxide and boron trifluoride dissolved in methyl alcohol, or in the form of the complex $(C_2H_5)_2O \cdot BF_3$.

The addition product of formic acid to monovinylacetylene, or *formoprene*, was studied in detail. Its constants are:

Boiling point 42° C. at 40 mm.; d_{20}^{20} 0.9867; n_D^{20} 1.4534; Exaltation 0.4

Molecular Weight Cryoscopic in benzene	Observed 100	Calculated 98
	Found %	Calculated for $C_6H_8O_3$ %
Carbon	60.99	61.22
Hydrogen	6.23	6.12
Oxygen	32.73	32.65

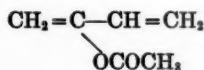
Condensation with maleic anhydride gave a crystalline product, melting at 161–2° C.; *semicarbazone*, melting 199° (decomposition). The condensation product corresponds in its composition to cyclohexanonedicarboxylic acid:



	Determined	Calculated for $C_8H_{10}O_3$
Carbon	51.11%	51.59%
Hydrogen	5.54%	5.41%
Oxygen	43.35%	42.99%
Acid number	598.8 mg.	600.1

Hydration with dilute sulfuric acid in the presence of mercury salts resulted in the formation of methylvinyl ketone, identified as semicarbazone. Formoprene resembles chloroprene in its properties. It polymerizes spontaneously at room temperature in 10 days, forming a rubber-like, elastic polymer.

The interaction of monovinylacetylene with acetic acid in the presence of the catalyst, $HgO + BF_3 \cdot O(C_2H_5)_2$, resulted in the formation of the corresponding *butadiene acetate*:



Boiling point 50–2° C. at 25 mm.; d_{20}^{20} 0.9761; n_D^{20} 1.448; exaltation 0.83.

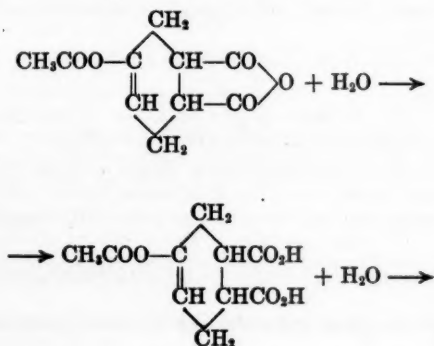
Molecular Weight	Found	Calculated for Acetoxybutadiene
Cryoscopic in benzene	111.5	112
Carbon	64.22%	64.22%
Hydrogen	7.45%	7.19%
Oxygen	28.31%	28.57%

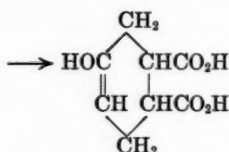
The structure was determined by condensation with maleic anhydride. The condensation product, recrystallized from water, melts at 169–71° C. (the product was evidently not quite pure); acid number 374; saponification number 526.4; ester number 175.

Calculated for the acid obtained from the condensation product of 2-acetoxy-1,3-butadiene with maleic anhydride, after saponification of anhydride: acid number 350; saponification number 526.4; ester number 175.

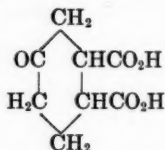
Thus, according to the resulting constants, the condensation product is evidently *acetoxytetrahydrophthalic acid*, partly contaminated by the products of saponified ester, *i. e.*, ketoacid. This is also supported by the low ester number.

Additional saponification in the presence of hydrochloric acid results in the corresponding ketoacid, cyclohexanonedicarboxylic acid, melting 161° C. Its composition was determined by combustion (see above). In fact, acetoxy-1,3-butadiene on condensation with maleic anhydride forms a product of the following structure:





This compound is unstable and isomerizes to the ketone:



Hydrogenation of Monovinylacetylene

(Work performed by L. G. Tzyurikh and Nankina)

Butadiene was obtained with 25–30 per cent yields by hydrogenation of monovinylacetylene in ethyl acetate in the presence of colloidal palladium precipitated on starch. Butadiene was also obtained from monovinylacetylene hydrogenation in the presence of nickel catalyst.

In this article a brief description is given of the fundamental work carried out at the SK Organic Laboratory of GIPKH. A detailed account of the experimental material will appear in a special issue.

Summary

1. A method is described for the continuous polymerization of acetylene at low temperatures in a dilute aqueous solution of the catalyst, $\text{CuCl} \cdot \text{NH}_4\text{Cl}$. Monovinylacetylene is obtained as the chief product of the reaction, with a 75–80 per cent yield, based on the acetylene entering into the reaction, and 25–30 per cent of trimers and higher polymers of acetylene as by-products. The conversion of acetylene by a single passage of the gas is 40 per cent. The yield, based on the acetylene, is nearly 100 per cent.

2. Data on the optimum amount of the catalyst are compiled, and the principal factors which affect the process of polymerization of acetylene with the formation of monovinylacetylene as the chief product are shown.

3. The problem of the mechanism of the polymerization of acetylene is discussed.

4. A method of separation and collection of the reaction products by absorption in solvents is described.

5. A method for the discontinuous synthesis of chloroprene without excess pressure is described.

6. A procedure for the continuous production of chloroprene from pure monovinylacetylene and its mixture with acetylene is described.

7. The conditions of the polymerization of chloroprene to α -polymer are described, with particular reference to the conditions which inhibit the formation of rapidly aging and hardening polymers. The latter are considered as balata-like products.

8. A process of polymerization in solvents, with formation only of the α -polymer is described.

9. Polymers of chloroprene were studied by ozonization and oxidation with

nitric acid. The first method was applied to α -, μ - and ω -polymers. Succinic acid was obtained as the chief reaction product, with nearly a theoretical yield based on the ozonized polymer. Oxidation with nitric acid results in the formation of succinic and oxalic acids. The latter is formed by a secondary oxidation of succinic acid.

10. The composition of acetylene trimers is described, including among them the hitherto unknown acetyldivinyl, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{C}\equiv\text{CH}$, which accompanies divinylacetylene. The physical and chemical properties of these trimers are given.

11. The polymerization of trimers and higher polymers for the production of synthetic varnishes and lacquers is briefly described.

12. Data on the action of alcoholic solution of alkalis on 2,4-butene-2 are given. The ethyl ether of 2-chloro-2-butene is the resulting reaction product.

The methods of the following syntheses are also shown:

(a) Chlorobutenol by the action of aqueous solutions of hydroxides and carbonates of alkaline and alkaline-earth metals.

(b) Dichlorobutenyl ether from chlorobutenol and 2,4-dichloro-2-butene. The xanthate of 2-chlorobutene-4-ol was also synthesized.

13. A series of new syntheses from monovinylacetylene is described:

(a) The synthesis of α,β -dichlorobutadiene, its structure and polymerization are described.

(b) The addition of aliphatic acids to monovinylacetylene in the presence of mercuric sulfate and mercuric oxide + boron trifluoride as catalysts, with the formation of the esters of 2-oxy-1,3-butadiene, is shown. The methods of synthesis and the structure of formic and acetic esters of 2-oxy-1,3-butadiene are also described. The condensation products with maleic anhydride and their hydration derivatives were prepared.

14. The condensation of methyl and ethyl alcohols with monovinylacetylene in alcoholic solutions of alkalis with the formation of 1-methoxy-3,4-butadiene and 2-ethoxy-1,3-butadiene, resp., are described.

15. The addition of methyl alcohol to monovinylacetylene in the presence of mercuric oxide and $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ as catalysts is described.

16. The formation of styrene by the polymerization of monovinylacetylene is reported.

17. The hydrogenation of monovinylacetylene to butadiene is described.

References and Footnotes

¹ Nieuwland, Calcott, and Downing, *J. Am. Chem. Soc.*, **53**, 4197 (1931).

² Ingold, *J. Chem. Soc.*, **1528** (1924).

³ With respect to the ionization of acetylene and its weakly acid properties, see Chavastelon, *Compt. rend.*, **125**, 245; Billitzer, *Z. phys. Chem.*, **40**, 535; *Monatsh.*, **23**, 199, 216; Küspert, *Z. phys.-chem. Untersuch.*, **17**, 292; Skossarewski, *Chem.-Ztg.*, **38**, 794 (1914); cf. also Mignonac et Saint-Annay, *Compt. rend.*, **74**, 959 (1929).

⁴ Chavastelon, *Compt. rend.*, **125**, 1034 (1897); **127**, 68 (1900); **130**, 1634, 1764 (1901); **131**, 48.

⁵ The continuous method of polymerization of acetylene in an aqueous solution of the catalyst, $\text{CuCl} \cdot \text{NH}_4\text{Cl}$, $\text{H}_2\text{O}-\text{HCl}$ is protected by Soviet Union patent applications Nos. 115,599/8414 and 120,130/8952 (1933).

⁶ Manchot, *Ann.*, **387**, 257 (1912).

⁷ The method of continuous removal of resinous substances from the reaction vessel by the use of solvents constantly withdrawn together with the dissolved resins, with resulting increase in the service of the reaction vessel and in the life of the catalyst, is protected by patent application No. 162,688/-13,365 (1935).

⁸ The process of continuous separation of the products of acetylene polymerization and their isola-

tion from the gas mixture by absorption in solvents is protected by patent application No. 118,845/8774 (1933).

⁹ Carothers, *J. Am. Chem. Soc.*, **54**, 4066 (1932).

¹⁰ The process of hydrochlorination of monovinylacetylene without pressure (as well as the possibility of carrying out the reaction in solvents) was protected by Klebanskiĭ, Trenke, Dolgopol'skii and Cheuichalova by patent application No. 134,771/10,752 (1933).

¹¹ Carothers, Williams, Collins, and Kirby, *J. Am. Chem. Soc.*, **53**, 4203, *et seq.* (1931).

¹² The process of polymerization in inert gases to prevent the formation of balata-like polymers is protected by Kelbanskiĭ, Dolgopol'skii, Margules, and Sorokina by patent application No. 134,772/10,453 (1933).

¹³ The process of polymerization to 100 per cent in solvents, with the formation of only α -polymer, is protected by the same investigators as above by patent application in 1934.

¹⁴ The work on polymerization was completed in January, 1934. In July, 1934, an American patent for the analogous method was issued.

¹⁵ Carothers, *J. Am. Chem. Soc.*, **56**, No. 5 (1934).

¹⁶ Lately the splitting-off of HCl from 2,4-dichloro-2-butene was successfully effected by conducting the latter over activated silica gel or Glukhovskii clay at 250–75° C., and also by the action of bases at high temperatures, with the formation of 25 per cent and more of chloroprene.

¹⁷ The process of production of α,β -dichloro-2,3-butadiene was protected by Klebanskiĭ and Vol'kenshtein by patent application No. 139,238 (1933).

¹⁸ Carothers, *J. Am. Chem. Soc.*, **55**, 2004 (1933); *Ind. Eng. Chem.*, **26**, 30 (1934).

¹⁹ The synthesis of 1-chloro-2-vinylacetylene was published by Carothers and Jacobson, *J. Am. Chem. Soc.*, **55**, 4669 (1933). This synthesis was performed by us long before the above publication appeared (cf. the report of the Laboratory of Organic Chemistry GIPKH for 1933).

²⁰ Favorskii, *J. prakt. Chem.*, **37**, 382, 1991; **44**, 208.

²¹ The formation of styrene in the polymerization of monovinylacetylene in an acid medium was performed before the work of Dykstra, *J. Am. Chem. Soc.*, **56**, 2729 (1934), but was not published.

²² Carothers, *Ibid.*, 1169 (1934).

²³ The synthesis of 2-formoxy-1,3-butadiene, 2-acetoxy-1,3-butadiene and its homologs, and the synthesis of methoxy- and ethoxybutadiene in the presence of the catalysts $\text{HgO} \cdot \text{BF}_3$, HgSO_4 or $\text{HgO} \cdot (\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3$, were protected by Klebanskiĭ, Trenke, and Rokhlina by patent application No. 127,476/9570 (1933) and additional application in 1934.

Investigation of the Structure of Rubber by Means of Electron Diffraction

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1. Introduction

The amorphous condition is a characteristic state of undeformed rubber. The x-ray diffraction picture of undeformed rubber is analogous to the patterns produced by liquids, and consists of 1-2 concentric amorphous rings. Synthetic chloroprene rubber gives an analogous diagram.

Katz¹ was the first to show that an x-ray diagram of stretched natural rubber contains interference points. With increasing stretching the intensity of these points increases, while the intensity of the amorphous rings decreases. It appears that the process involves the formation of crystallites, oriented in a definite manner, which give a diagram of the fiber structure (fiber diagram), as in the case of drawn and rolled metals.

Mark and von Susich² and Meyer and Mark,³ from their studies of stretched samples of rubber in two mutually perpendicular positions, came to the conclusion that the unit cell of the crystallite is orthorhombic, with the axes $a = 12.3$, $b = 8.3$, and $c = 8.1$ A. U., corresponding to the direction of elongation.

There is no definite information available on the structure of synthetic chloroprene rubber. It is, however, known from the investigation of Kenney⁴ that stretched chloroprene rubber also shows a fiber structure and that the identity period in the direction of elongation is 4.9 A. U.

For a more detailed study of the rubber structure, it would be desirable to obtain interference diagrams of highly oriented preparations. Such a high orientation could probably be obtained with rubber films of about 10^{-6} cm.

It might be expected that the diffraction diagrams obtained by passing electrons through such thin films of rubber would show a spotty character, corresponding to the true orientation of groups of rubber molecules in thin layers.

2. Diffraction of Electrons by Passing Through Thin Layers of Natural Rubber

The first observations were made with pale crepe rubber. A film of the required thickness was prepared in the following manner. A drop of a weak solution of rubber in benzene was allowed to spread on a water surface, leaving, after evaporation of the solvent, a film of 10^{-6} cm. thickness. This film was transferred to a brass plate with a suitable perforation, and the whole, after evaporation of the water, was placed in the apparatus for examination. The assembly was so constructed that parallel diffraction pictures of rubber and gold could be obtained. With the aid of the latter the wave-length of the electron beam was measured. This procedure made it possible to measure the wave-length with an accuracy of 0.1 per cent. In these experiments λ varied within the limits of from 0.0635 to 0.0695 A. U.

After the passage of the electron beam through the rubber film, the resulting

debyeograph usually showed a diffraction picture in the form of three amorphous rings (Figs. 1 and 2).

Because of the sharp drop in the intensity of the rings and the difficulty of obtaining clear reprints with the reproduction of all three rings, only two reproductions are shown: Figure 1 obtained with the

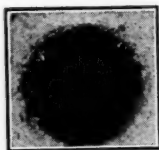


Figure 1
Electronograms of Unstretched Pale Crepe



Figure 2

exposure required for the development of the third ring, and Fig. 2 at a shorter exposure showing the development of the first and second rings with the third ring undisclosed. The ring diameters are 6.1, 12.3, and 20.2 mm., with identity periods of 4.15, 2.05, and 1.25 A. U., resp. It may be concluded from this that the second ring is the second order of the first one. The identity period 1.25 A. U. closely approaches the distance between some carbon atoms in the carbon chain (*cis*-configuration) of the rubber molecule.

Thus in the films showing a diffraction pattern of three amorphous rings, there is a complete disorder of orientation of the rubber crystallites. Only in some cases the inner amorphous ring discloses localized interferences resembling the fiber diagram and indicating a certain orderly arrangement of crystallites.

Since amorphous rings give only limited information on the structure of rubber, it was desirable to obtain a preparation with a higher orientation of crystallites suitable for a more thorough study.

It is known from the investigations of Katz¹ that stretching leads to an orderly arrangement of crystallites in rubber. Conducting x-rays through a stretched rubber film results in a fiber diagram. An analogous process could be expected by passing an electron beam through a stretched rubber film. The experiments showed that it is actually possible to obtain fiber electronograms.

It was observed that the intensity of the spot interference is far greater directly after placing the film in the apparatus, and that with lapse of time, under the action of the electron beam (temperature effect), a reversion of the rubber to the amorphous condition takes place, attended by disappearance of the spot interference. A similar effect of an electron beam on stretched rubber was observed by Trillat and Motz.⁴ Thus in order to obtain a more sharply defined picture it was desirable to produce the electronograms of stretched rubber directly after stretching, i. e., to cause stretching of the film during the passage of an electron beam through it.

This was effected in the following manner. Two bent wires 1 mm. in diam. are fastened to the two concentric ground joints, as shown in Fig. 3. The top ground joint is directly fitted by means of grease to that part of the apparatus which corresponds to the usual position of the object to be examined in the path of electron beam. By turning the ground joint I to the left and the joint II to the right, the wires are twisted in opposite directions. Before the experiment is started, the joint I is withdrawn, the rubber film is lifted from the water surface onto the wires set at 1 mm., which gives a film of 1 mm. width, the joint I is returned into the place set in this position, and the air is pumped out of the apparatus in the usual way.

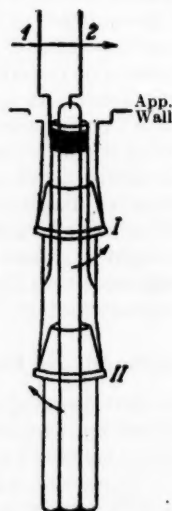


Figure 3

By turning joint *I*, it is possible to set the film in the path of the electron beam and to obtain a diffraction picture of the unstretched rubber. By turning simultaneously joints *I* and *II* in opposite directions, the wire ends are diverted and, if the operation is successful, the film is stretched, without breaking, in the direction indicated by an arrow in the drawing. The diffraction of the stretched rubber film can then be observed.

The film was stretched about 800 per cent, giving an extremely thin object of high crystallite orientation. For the production of a fiber diagram less stretching is sufficient, while high elongations give points of greater intensity. The diffraction picture then shows the clearly defined character of a fiber diagram (Fig. 4).

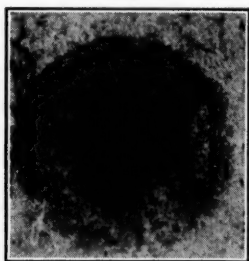


Figure 4—Electronogram of Stretched Pale Crepe



Figure 5—Scheme of Electronograms of Stretched Pale Crepe

The resulting electronograms show, together with the amorphous rings, a large number of spots, the small and unequal intensity of which makes it impossible to obtain a detailed reproduction. A scheme of the arrangement of the spots is given in Fig. 5.

The appearance of nearly all the points can be explained by the model of the elementary cell of rubber constructed by von Susich, Mark, and Meyer (orthorhombic symmetry with axes $a = 12.3$, $b = 8.3$, and $c = 8.1$ Å). If it is assumed that all crystallites of a stretched rubber film are so arranged that the axis c is pointed in the direction of the stretching and lies together, with the axis a , in the plane of the film, then the axis b is situated perpendicular to the plane of the film. Of course, a certain imperfection in the orientation of crystallites with possible reflection from the planes of zone (010) must be assumed. The isoprene chains are here arranged parallel to the film plane. The diagram also shows the indexes of planes, causing one or another reflection.

The electronograms show also a number of spots, the appearance of which can be explained by the rubber model; these, however, could not be included in the diagram because of their low intensity. All the points shown are surrounded by the third ring with identity period 1.25 Å. U., which contains four symmetrical localized interference maxima as can be clearly seen in Fig. 4. In the same figure appear points in the second ring, while the inner ring, also containing interference spots, is strongly overexposed. Separate points are blurred, forming a line. This phenomenon can also be explained by some arbitrariness in the arrangement of chains.

3. Comparison of the Results with Those Obtained by Other Investigators

A comparison of the results with those obtained by Trillat and Motz⁴ and Bruni and Natta⁵ shows that the identity periods 4.15 and 2.05 Å. U., corresponding to

the first two amorphous rings, agree very closely with the identity periods 4.08 and 2.04 A. U. determined by Bruni and Natta for the same rings. The second amorphous ring is explained by them in exactly the same way as the second order of the first ring. Thus complete agreement exists in the results of this part of the investigation.

In regard to the third amorphous ring, there is some divergence. The identity period 1.25 A. U. for the third ring does not agree with that of 1.399 A. U. obtained by Bruni and Natta, and, therefore, contrary to their idea, cannot be explained as the third order of the first ring. We believe that this period of identity corresponds to the distance of 1.2 A. U. between the carbon atoms in the carbon chain of the rubber molecule.

This difference in the results may be explained by the fact that the third amorphous ring, obtained by these investigators, was considerably blurred. This causes relatively great errors in the calculation of the identity period of the third ring. The ring obtained by us is so sharply defined that the digression of the third identity period (1.25 ± 0.03 A. U.) from the magnitude of the third order 1.38 A. U. cannot be explained by experimental error. In respect to spot interferences, the work of Bruni and Natta shows some inconsistency.

In this work the authors claim that the pattern obtained by them can be explained by the model of the elementary cell of rubber constructed according to the x-ray analysis. To the interference points with the identity periods 9.16, 4.58, 1.16, 8.25, 4.22, and 2.1 A. U., they ascribe the indexes of dispersion planes: (010), (020), (080), (001), (002), and (004). It is evident that in ascribing these indexes to the interference points, Bruni and Natta used the orthorhombic model of rubber with the axes $a = 12.3$, $b = 9.3$, and $c = 8.3$ A. U. This position, however, does not correspond to the model of the elementary rubber cell, constructed by von Susich, Mark, and Meyer, with $a = 12.3$, $b = 8.3$, and $c = 8.1$ A. U. Thus a considerable difference exists between the results obtained by the x-ray analysis of Bruni and Natta and those of many other investigators. It should be noted that in some publications, e. g., in the book of Mark and Meyer (*The Structure of High Poly-molecular Organic Natural Compounds*), the value is erroneously given: $b = 9.3$ A. U.

The indexes of planes given by Bruni and Natta cannot be ascribed to the interference points of stretched rubber obtained by us. The indexes, shown in Fig. 4, correspond to the rubber model of orthorhombic symmetry with the axes: $a = 12.3$, $b = 8.3$, and $c = 8.1$ A. U. These values agree with those obtained by x-ray analysis. The interference points with the indexes 200, 300, 400, 201, and 202 agree in position with the interference points obtained by Trillat and Motz.⁴ These investigators ascribe to them the indexes 020, 030, 040, 120, and 220, assuming evidently that the axis a lies in the direction of the stretching, that the axis b is situated in the plane of the film, and that the axis c is perpendicular to it. By such a selection of axes the values for the sides of the elementary cell are: $a = 8.1$ and $b = 12.3$ A. U. This is somewhat inconsistent with the previously accepted designations and the resulting values of $c = 8.1$ and $a = 12.3$ A. U.

Besides the interference points with the given indexes, as shown in Fig. 5, our electronograms contain higher orders of reflection, which confirms the structure of the elementary rubber cell with the axes: $a = 12.3$, $b = 8.3$, and $c = 8.1$ A. U.

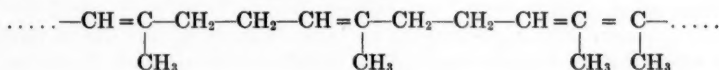
The electronograms show also a small number of spots, which cannot be explained by the model of the oriented rubber. References to this phenomenon can be found in the articles by Trillat and Motz. The causes of this phenomenon are being investigated.

It should be noted that the spot interference of natural rubber is obtained, as a rule, only with stretched samples. Unstretched films only occasionally give

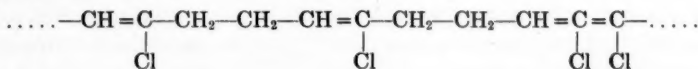
localized interferences or maxima in the inner ring, which are probably caused merely by the tension in the process of removing the film from water or drying of the sample. The spot interference of unstretched rubber film obtained by Bresler, Strauff, and Zelmanov,⁷ is probably explained by these causes.

4. Investigation of Synthetic Chloroprene Rubber by Means of an Electron Beam

The chemical formula of natural rubber is:



Chloroprene rubber differs from natural rubber by the substitution of Cl for the CH_3 groups.



The chloroprene rubber molecule is also a chain, and its structure must be fundamentally analogous to that of natural rubber, except for those changes which are caused by the substitution of chlorine for methyl groups.

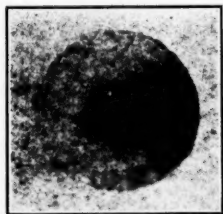


Figure 6—Electronogram of Chloroprene Rubber

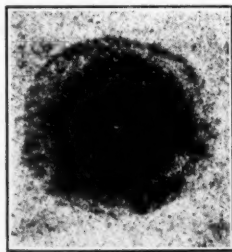


Figure 7—Magnified Central Part of Electronogram of Chloroprene Rubber Shown in Fig. 6

Films of chloroprene were obtained by evaporating its solutions in carbon tetrachloride on a water surface.

On passing an electron beam through the film, a diffraction picture was obtained, which showed dark spots, in many cases, besides fairly sharply defined rings, thus indicating the presence of crystallites of considerable size (Figs. 6 and 7). It should be noted that, whereas natural rubber gives spot interference only when its film is stretched, chloroprene rubber gives this interference in sharply defined form without any external stress on the sample. The number of these spots in various cases was either two diametrically opposed, or four forming a true right angle, or six, as can be seen in the photograph (Figs. 6 and 7). The six points are distributed in the two rings, two points in the large ring and four points in the smaller ring; this indicates the presence of two different identity periods, *i. e.*, two different systems of planes of reflection. The identity periods, determined from nine negatives obtained at various λ , are equal (4.06 ± 0.4) and (4.52 ± 0.04) A. U.

For the electronogram with only two spots the identity period is 4.06 A. U., and

for that with four spots it is 4.52 A. U. Thus the case of six points is more general while that of two and four points is a special case, *viz.*, when the orientation causes the destruction of either two or four points. Trillat and Hirsch⁸ obtained analogous results in the study of the diffraction of paraffin. They also observed that by turning the film by 15°, there was formed instead of the Debye-Scherrer rings a diffraction pattern of two spots situated on the vertical center line. This phenomenon confirms the theory of complete orientation of crystallites in the film.

For understanding the interference pattern, it is sufficient to examine the more general case of six points.

If their appearance is explainable in the same way as in the case of stretched natural rubber by the diffraction of orderly distributed crystallites, the elementary cell of which is determined by the von Susich model, *i. e.*, possessing rhombic form with the edges $a = 12.3$, $b = 8.3$, and $c = 8.1$ A. U., then it follows that the position of two points is satisfactorily explained by the dispersion of the plane (020) ($\sin^2 \vartheta = 0.0000698$ at $\lambda = 0.0688$ A. U.; calculated $\sin^2 \vartheta = 0.0000690$). The position of four points, however, cannot be explained. The value determined for them is $\sin^2 \vartheta = 0.0000570$, while the nearest value of \sin^2 , derived from the von Susich model, is 0.0000666 of the plane (211) and 0.0000493 of the plane (201). Thus it is necessary to assume that the elementary cell of chloroprene rubber has the same form as that of natural rubber, but with different dimensions of its edges. Supposing that, like natural rubber, the crystallites are distributed in the film in such a way that the two axes of the elementary cell lie in the plane of the film and the third one perpendicular to it, it is possible to ascribe indexes to the reflecting planes for four (210) and for two points (020). By using the formula of the rhombic symmetry:

$$\sin^2 \vartheta = \frac{\lambda^2}{4} \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right), \quad (1)$$

it is possible to construct two equations for the determination of the magnitudes of the edges a and b :

$$0.0000698 = \frac{(0.0688)^2}{4} \times \left(\frac{4}{b^2} \right); \quad (2)$$

$$0.0000570 = \frac{(0.0688)^2}{4} \times \left(\frac{4}{a^2} + \frac{1}{b^2} \right). \quad (3)$$

From these two formulas are determined $a = 10.93$ and $b = 8.23$ A. U. The magnitudes of the axes b of the elementary cells of chloroprene and natural rubbers agree within the limits of permissible error. The edge a is changed from 12.3 to 10.93 A. U. The shortening of the edge a can be explained by the substitution of Cl for the CH_3 group in rubber.

In addition to the six intense points, some electronograms show also a certain number of less intense spots distributed on two peripheries; their calculated identity periods are 2.03 and 2.71 A. U., resp. From the magnitudes obtained for a and b , their position in the electronogram is well determined by the dispersion planes with the indexes (420) and (030).

The synthetic chloroprene rubber was furnished by the Leningrad Sovprene factory. We have obtained recently electronograms of the chloroprene rubber manufactured by E. I. Du Pont de Nemours and Co. Some of these electronograms are interesting because of the presence of a large number of spots, all of which can be arranged on four circles, the radii of which are determined by the given identity periods at 4.06, 4.52, 2.03, and 2.71 A. U. On close examination it becomes convincingly evident that a combination of all these points is formed, if it is postulated

that the crystallites, on distribution in the plane of the film with one of the axes perpendicular to the film surface, still possess one degree of freedom of revolving about this axis. Thus the electronogram consists of six points with differently directed axis of symmetry, but situated in the pattern plane.

Proceeding from the determined magnitude of the edges a and b , and on the assumption that the identity period of 4.9 A. U., obtained by Kenni⁴ by x-ray analysis, represents the third side of the elementary cell, it is possible to compute its volume: $9.8 \times 10.93 \times 8.23 = 882 \text{ \AA}^3$, and from this, if the density of chloroprene rubber is assumed to be $\delta = 1.23 \text{ A. U.}$, it is possible to determine the number of chloroprene residues in the elementary cell:

$$Z = \frac{V \times \delta}{ML} = \frac{882 \times 1.23}{88.5 \times L} = 7.4,$$

where M is the molecular weight and L is the mass of hydrogen atom.

The resulting value is equal to that obtained in the calculation of the isoprene residues of natural rubber. Figure 7 is incompatible with the acceptable numerical data in the rhombic system, and, as in the case of natural rubber³ must be replaced.

In addition to the six points, the electronogram of chloroprene rubber contains somewhat sharply defined amorphous rings with identity periods of 2.23, 1.47, and 1.18 A. U.

The first amorphous ring can be ascribed to the reflection of the second order from the planes. The second and third rings correspond to the distance between the carbon atoms 1.5 and 1.2 A. U. in the carbon chain of the molecule of chloroprene rubber. The explanation of the interferences of higher orders may serve as a final confirmation of the proposed theory of the magnitude of the elementary cell of chloroprene rubber.

The corresponding electronograms recently obtained are being investigated.

5. Conclusions

1. Irradiation of unstretched rubber with an electron beam gives electronograms in the form of three amorphous rings with identity periods of 4.15, 2.05, 1.25 A. U. The third identity period closely approaches the distance between the carbon atoms of the carbon chain of a rubber molecule.

2. An electronogram obtained by the irradiation of stretched rubber with an electron beam discloses interference points, and the whole pattern has the character of a fiber diagram.

3. An electronogram contains more details (rings, points) than the corresponding x-ray diagram. Thus electron analysis makes it possible to obtain more information relating to the structure of rubber, and in this respect has an advantage over x-ray analysis.

4. Calculation of the electronograms shows that the elementary cell of rubber has orthorhombic symmetry with edge dimensions of $a = 12.3$, $b = 8.3$, $c = 8.1$ A. U. These results agree with the model of the elementary cell of rubber constructed by von Susich, Mark, and Meyer on the basis of x-ray analysis.

5. Highly oriented rubber preparations give in addition to a large number of points, a certain number of spots which do not fit into the scheme of points of oriented rubber. This phenomenon requires a further study.

6. Spot interference appears, as a rule, only with stretched films. The localized maxima on the interference rings of irradiated unstretched films observed in some cases are explained by a partial orientation formed in the process of drying the film.

7. The irradiation of chloroprene rubber by an electron beam also gives spot interference; this can be obtained without any external action upon the film.

8. The position of the interference points on the diffraction pattern is explainable on the assumption that the model of the elementary cell of chloroprene rubber has an orthorhombic symmetry with axes $a = 10.98$, $b = 8.23$ A. U.

9. A calculation of the number of chloroprene residues in the elementary cell of chloroprene rubber gives a value of 8.

10. Some samples of Duprene gave electronograms in the form of a large number of points. The combination of points is formed from the spots of the usual electronogram by its rotation about the axis perpendicular to the pattern plane. This phenomenon can be explained by the corresponding orientation of crystallites in the sample.

11. The electronogram of chloroprene rubber contains also three amorphous rings, with identity periods of 2.23, 1.47, and 1.18 A. U. The last two closely approximate the distance between the carbon atoms of the carbon chain of the chloroprene molecule.

Acknowledgment

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X-Ray Study of Amorphous Rubber

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Introduction

Previous x-ray work on rubber¹ has shown that unstretched rubber gives a distinctly amorphous pattern, while rubber stretched several hundred per cent gives a typically crystalline pattern. Although considerable work has been done on the interpretation of the x-ray results for stretched rubber, no serious attempt has been made to analyze the amorphous pattern. It is the purpose of this paper to present a Fourier analysis of the x-ray scattering curve for unstretched rubber, and to discuss critically the amount of information concerning the structure of unstretched rubber which can be deduced from the amorphous pattern. By using the new method of Fourier analysis, one gets directly from the x-ray scattering curve the distribution of neighboring atoms about any given atom, without making any *a priori* assumptions as to crystallinity or the nature of the molecule.

Experimental

The diffraction patterns were made in a cylindrical camera of radius 4.40 cm. using $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiation. To eliminate background corrections, the radiation was monochromatized by reflection from a rock salt crystal, and the camera evacuated to eliminate air scattering. The sample was a cylinder of smoked sheet² of diameter 1.5 mm. The microphotometer records of the $\text{CuK}\alpha$ and $\text{MoK}\alpha$ patterns were changed to intensity curves in the usual way. The two curves were corrected for polarization and absorption and then fitted together. At small values of $\sin \theta/\lambda$ the Cu curve was considered the more reliable, while at the larger values, the Mo curve showed more detail and was therefore given the greater weight. The final intensity curve, corrected for polarization and absorption, is shown in Fig. 1A, plotted against $\sin \theta/\lambda$.

Fourier Method Applied to Rubber

The application of Fourier analysis to the x-ray scattering patterns of crystalline or non-crystalline materials has been described in previous papers.^{3,4} For a material containing only one kind of atom, the weighted average density of surrounding atoms is given by the relation

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \left(\frac{2r}{\pi}\right) \int_0^\infty s i(s) \sin rs \, ds \quad (1)$$

where $4\pi r^2 \rho(r) \, dr$ is the average number of atoms between r and $r + dr$ from any atom.

- ρ_0 = average density of sample in atoms per unit volume.
- $s = 4\pi \sin \theta/\lambda$
- $i(s) = (I/N - f^2)/f^2$
- I/N = unmodified intensity per atom in electron units.
- f = atomic scattering factor.

The composition of the sample was taken to be C_6H_8 . Relative to the carbon atoms the unmodified scattering from the hydrogens can be neglected. In applying the Fourier method we therefore consider the sample as made up of carbon atoms alone. The unmodified scattering per atom is taken as f_c^2 , and the modified scattering per atom as the modified scattering per carbon plus eight-fifths the modified scattering per hydrogen. The modified and independent unmodified scattering⁵ per carbon atom are given by curves C and D of Fig. 1. The total independent scattering per carbon atom is given by curve B. At large angles the scattering curve of

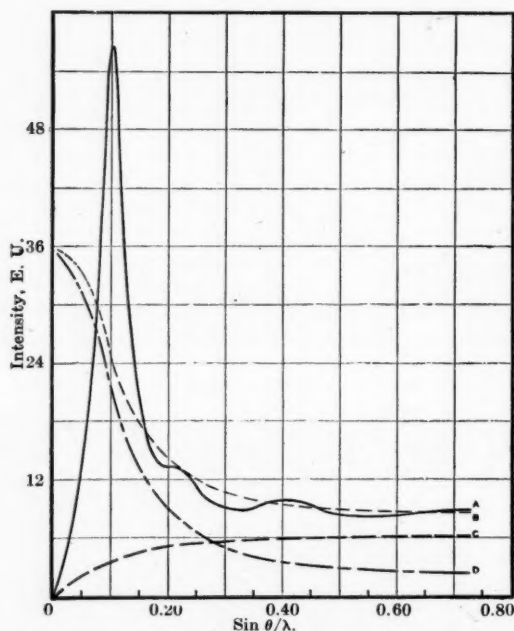


Figure 1—A, Experimental Intensity Curve for Unstretched Rubber; B, Total Independent Scattering per Carbon Atom; C, Modified Scattering per Carbon Atom; D, Independent Unmodified Scattering per Carbon Atom

any material approaches independent scattering. The experimental intensity curve A, which is at first in arbitrary units, is therefore drawn to a scale that it approaches curve B at large angle. This serves to put the experimental curve A upon an absolute basis, electron units per atom. The curve $i(s)$ is then given directly in absolute units by subtracting B from A and dividing through by curve D. The integration involved in equation (1) is readily carried out on the curve $si(s)$ by means of a Coradi harmonic analyzer. Taking the density of unstretched rubber as 0.94 one obtains for ρ_0 the value 0.042 carbon atoms per \AA^3 .

The resulting radial density curve $4\pi r^2\rho(r)$ is given in Fig. 2a. The curve represents the average number of carbon atoms at any distance r from any carbon atom. The area under the curve gives directly the number of carbon atoms in a particular range of distance. Figure 2b gives the differential density, that is, the difference between the actual atomic density and the average density.

Discussion of Results

From Fig. 2 one finds that on the average each carbon atom in rubber has 1.98 carbon neighbors at a distance of about 1.52 A. U. Beyond these nearest neighbors come approximately 3.4 carbon atoms at an average distance of 2.68 A. U. Beyond these come further concentrations at about 4.0 and 5.0 A. U. It might be pointed out that this much information is obtained directly from the x-ray scattering curve without making any assumptions as to the structure of the sample.

The results are in quite satisfactory agreement with the present picture of rubber as comprised of long chain molecules. Figure 3 represents schematically a section of the chain. The single bond C—C distance is taken as 1.54 A. U. and the double bond C—C distance as 1.38 A. U. The bond angles are taken as $109^{\circ}28'$ and $125^{\circ}16'$. Regardless of free rotation about the single bonds, and consequent bending and coiling of the chain, the nearest and next nearest neighbor distances are perfectly definite.

TABLE I. FIRST NEIGHBORS

Atom	No. of Neighbors and Distance, A. U.	
1	2—1.54	
2	2—1.54	1—1.38
3	1—1.54	
4	1—1.54	1—1.38
5	2—1.54	

Average 2.0 first neighbors at distance 1.51 A. U., in good agreement with the first peak of Fig. 2.

TABLE II. SECOND NEIGHBORS

Atom	No. of Neighbors and Distance, A. U.	
1	1—2.59	2—2.52
2	1—2.59	1—2.52
3	1—2.59	1—2.52
4	2—2.59	1—2.52
5	1—2.59	1—2.52

Average 2.4 second neighbors at distance 2.56 A. U. Of the third neighbor distances the separation between atoms 1 and 5 has the definite value 3.13 A. U. The remaining third neighbor distances depend upon the orientation about the single bond directions, and vary between a minimum of 2.56 A. U. and a maximum of 4.04 A. U. The second peak of Fig. 2 is only partially resolved on the right-hand side, and therefore includes the 2.4 second neighbors at a distance 2.56 A. U. plus the nearest of the third neighbors.

The third peak of Fig. 2 occurring at about 4.0 A. U. is evidently due to the more distant third neighbors. The striking correspondence between this peak and the third neighbor peak of a normal hydrocarbon is clearly brought out by comparing Fig. 2b with the density curve for *n*-heptane.⁶ The first three peaks of Fig. 2 are thus completely explained by the usual picture of rubber as comprising long chain molecules.

The fourth peak of Fig. 2 occurs at a little more than 5 A. U. This concentration represents an atom's nearest carbon neighbors in other chains, the distance from a carbon atom in one molecule to the first concentration of carbon atoms in neighboring molecules being of the order 5 A. U. It may be of interest to point out that it is primarily this concentration of scattering matter which is responsible for the very

strong peak at $\sin \Theta/\lambda = 0.104$ in the experimental intensity curve. The fact that so many organic liquids, such as benzene, cyclohexane, paraffin, rubber, etc., give a strong diffraction ring at just about the same value of $\sin \Theta/\lambda$ is simply due to the fact that there is a fairly definite closest distance of approach of carbon atoms in different molecules.

From the analysis of the x-ray pattern of amorphous rubber only two conclusions can be drawn:

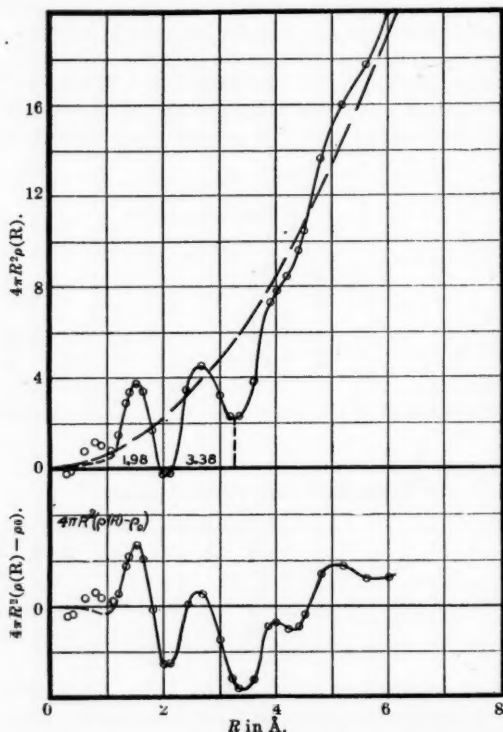


Figure 2—(a, upper) Radial Density of Surrounding Atoms in Unstretched Rubber. (b, lower) Differential Radial Density of Surrounding Atoms in Unstretched Rubber

1. The x-ray pattern and the resulting density curve are completely explained by the usual chain molecule picture of rubber. It is not necessary to make any specific assumptions as to mutual orientation of the chains.

2. Since no assumptions are necessary, it follows that from the analysis of the amorphous rubber pattern one gets practically no information as to relative orientation of the chains or as to whether the individual chains are straight or coiled. Any specific conclusions which have been drawn from the amorphous pattern of rubber as to the configuration of the chains can have but little significance.

Summary

The density of surrounding atoms in unstretched rubber is determined by a

Fourier analysis of the x-ray scattering curve. The resulting distribution curve is in good agreement with the usual picture of rubber as comprised of long chain molecules. It is concluded that but little information can be obtained as to the configuration of the chains in unstretched rubber.

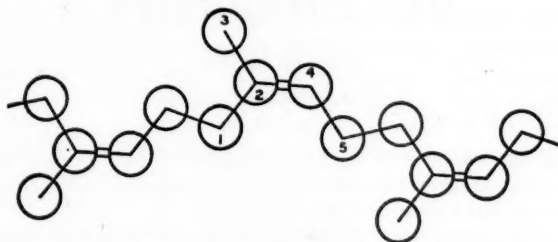


Figure 3—Schematic Representation of Long Chain Molecule in Rubber

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Inorganic Substances with Rubber-like Properties

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Two inorganic substances with elasticity similar to that of rubber are described in the literature of the subject, *viz.*, elastic sulfur and polyphosphonitrilic chloride. In this paper we shall deal with investigations of both.

It is common knowledge that sulfur heated to 170° becomes highly viscous; if then cooled, *e. g.*, by plunging into water, it yields an amorphous elastic product.

If threads of this amorphous product are stretched, they show a double refraction, and, as Trillat¹ has found, develop a fiber-diagram. With Go the author² has examined this diagram, and deduced from it the following arrangement of the sulfur atoms: long chains of sulfur atoms, linked by strong homeopolar valences, are

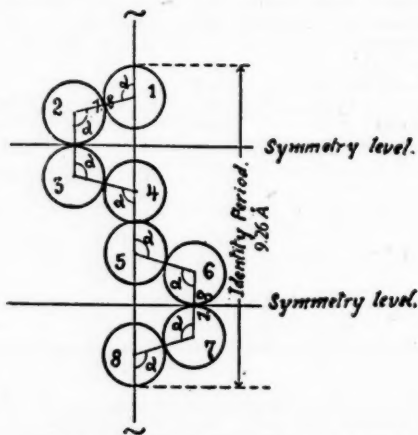


Figure 1—Arrangement of Atoms in the Elastic Sulfur

arranged parallel to the direction of stretching. Their special position in the elementary cell is shown in Fig. 1.

In a recent publication, Warren³ has made it clear that ordinary sulfur is made up of 8-atom rings. The molecular weight of the elastic form S_n is not known, but seems to be very high.

We know from earlier work that the melting of sulfur produces an equilibrium between the two forms, and this shifts, at higher temperatures, in favor of the chain-sulfur. About 1000 calories per gram atom S are consumed in the transformation of S_8 into S_n .

Endothermic reactions can proceed only if there is at the same time an increase in entropy—in other words, if the atoms, in the endothermic form, have more room to oscillate, that is to say, have a greater "phase-volume." During the process of

transformation, however, there is no increase in volume, but, on the contrary, a slight decrease; this, therefore, can be explained only on the ground that the sulfur atoms in the chain are more mobile than those in the rings. In view of this, the chains must be flexible. This entirely agrees with our conception of the nature of elasticity, which has recently been published.⁴

Some light is thrown upon the kinetics and mechanism of the polymerization and depolymerization of sulfur $S_8 \rightleftharpoons S_n$ by the following facts, some of which were already known, while others have been only lately observed by Sievers. Both polymerization and depolymerization are catalyzed by light; this indicates that S_8 molecules are split up by a quantum and then, in the manner of a chain reaction, unite with other sulfur rings, whereupon the product then formed becomes active, and is capable of splitting up other rings and attaching them to the rapidly growing chain. Conversely, a completed chain in a metastable state may be expected to disintegrate rapidly as soon as activation takes place at any point.

If purified sulfur is heated in pyrex glass vessels, it remains a thin fluid up to 172° , or a few degrees higher if in the dark. Above that point, it changes quite suddenly into an orange-colored resinous substance, and during that process the temperature falls by about 1° . If now carefully cooled, the resinous substance quickly liquefies again, and, when it is re-heated, the transformation into the resinous substance takes place at a lower temperature and more gradually. If this process is repeated, the transformation becomes more gradual every time, and all the phenomena of retardation disappear. The metastable fluid state, which is easily obtainable in virgin sulfur at 170° , can no longer be secured. The explanation, we think, is that in the process of heating active molecules, on which chains form very rapidly, appear only at relatively high temperatures; in the process of cooling the chains break away but leave nuclei which, on re-heating, quickly establish equilibrium (formation of chains).

The polymerization of metastable virgin sulfur at 170° can also be initiated by the addition of a very small quantity of polymerized product or product in process of polymerization.

If sulfur is heated to much higher temperatures (about 300°), its viscosity decreases and it turns brown. If it is then cooled, the viscosity rises again, but not up to the maximum that is reached at a temperature of 200° on heating virgin sulfur. If cooled still further it slowly liquefies; on heating thereafter it quickly becomes viscous, but never acquires the high viscosity of heated virgin sulfur.

Hence it would seem that at high temperatures the long chains break up into a large number of shorter chains, which are more stable than the long chains of virgin sulfur. Possibly in the process of cooling, they leave behind such a large number of nuclei that on re-heating a large number of short chains are formed instead of a small number of long ones.

The viscosity of highly viscous sulfur is greatly diminished by addition of traces of halogen or of hydrogen sulfide; at the same time the amount of S_8 in the equi-

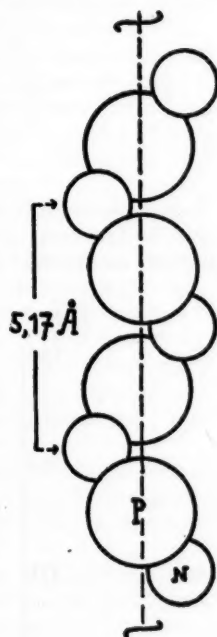
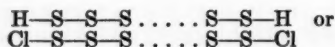


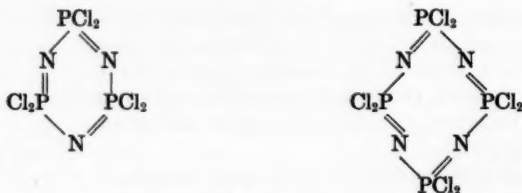
Figure 2—Probable Arrangement of the P and N Atoms in Polyphosphonitrilic Chloride

brated mixture becomes smaller. We think that shorter chains with Cl, Br, I, or H at the ends are formed:



These phenomena show that the polymerization of sulfur is to be regarded as similar to that of other reactions of polymerization.

The second elastic substance is polyphosphonitrilic chloride, discovered by Stokes,⁶ which is produced by heating various phosphonitrilic chlorides of low molecular weights, namely, the annular compounds:



Polyphosphonitrilic chloride is almost indistinguishable, externally, from slightly vulcanized rubber. Under tension it develops a double refraction and yields a fiber diagram, as Pankow⁶ has discovered. This diagram shows a fiber period of 5.17

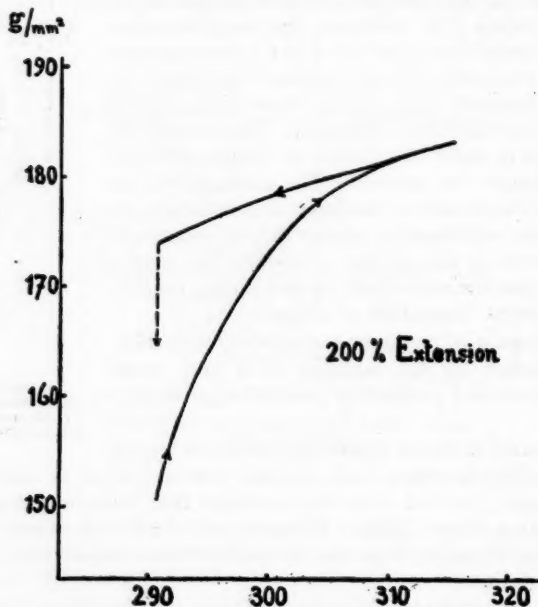


Figure 3—Stress-Temperature Curve of $(\text{NPCl}_2)_3$ at 200 Per Cent Extension

A. U. and in the direction of the fibers a diagonal screw axis. The most probable arrangement of the P and N atoms is shown in Fig. 2, which is based upon the x-ray diagram, the diameters of the P and N atoms, and the angles known from compounds such as POCl_3 and NH_3 .

Here again, as in sulfur or stretched rubber, long chains of primary valency are arranged parallel to the direction of tension. The space of one identity period in the axis is occupied by two PNCl_2 residues. When the tension is withdrawn, the interferences disappear. Cooling in the tense state causes the crystallized state to "freeze stiff," as in the case of rubber or fibrous sulfur.

We have also plotted the load-extension curve of this inorganic rubber. Phenomena of plastic flow are superposed on the phenomena of elastic deformation; on the whole, this curve resembles that of rubber. We have investigated them with reference to the temperature-tension curve of a stretched test-piece, and the curve is also wholly analogous to that of rubber (Fig. 3).

On heating, at a constant degree of deformation, the tension increases, and more than would be proportionate to the absolute temperature. The reason is that crystallized portions "melt" and also undergo tension. On cooling the tension remains at first higher than in the process of heating and decreases proportionately to temperature; it gradually continues to decrease also at constant temperature. The substance enters at first into the amorphous "under-cooled, metastable state," and crystallization and the restoration of the original degree of tension takes place only gradually.

Definite information as to the mechanism of contraction can be drawn from this temperature-tension curve. Contraction is produced, not by the action of attractive forces, but by the thermal agitation of the links of the flexible chains, which tends to produce the statistically preferred condition in which the chains are completely disoriented, in comparison with the less probable oriented arrangement.⁷

We are not as yet in a position to make any statement on the kinetics and the equilibrium of the polymerization of (PCl_2N) . Hemmi has found, however, that the reaction is reversible—depolymerization sets in slowly at low temperatures under the influence of specific chemicals, such as dioxane. A mixture of the phosphonitrilic chlorides of lower molecular weights is thus obtained.

The same considerations apply here as in the case of sulfur. If endothermic polymerization is to be possible, the atoms or groups of atoms in the polymeric product must have a greater phase-volume—i. e., greater mobility—than in the rigid annular trimer or tetramer. Hence the chains must be flexible.

It will be seen that there are strong analogies between the two inorganic and highly polymeric substances and the organic polymers, both in the morphological arrangement of the atoms and in the manner of their polymerization.

References

- ¹ 1932 (4), 51, 248.
- ² *Helv. chim. acta*, **17**, 108 (1934).
- ³ *J. Chem. Physics*, **3**, 6 (1935).
- ⁴ *Helv. chim. acta*, **18**, 570 (1935).
- ⁵ *J. Am. Chem. Soc.*, **17**, 275 (1895); **19**, 782 (1897).
- ⁶ *Compt. rend. Soc. phys. hist. nat. Genève*, Juillet, 1935.
- ⁷ Cf. the theory of elasticity of rubber given by Meyer, Valko, and Ferri, *Kolloid Z.*, **59**, 208 (1932); *Helv. chim. acta*, **18**, 570 (1935).

Plasticization of Rubber

T. L. Garner and C. M. Blow

The effect of oxygen in the mastication process of raw rubber has been demonstrated by Cotton (*Trans. Inst. Rubber Ind.*, 6, 487 (1931) and Busse (*Ind. Eng. Chem.*, 24, 140-146 (1932), who obtained a considerable reduction in the rate of plasticization of raw rubber when milled in the absence of oxygen. In a recent paper (Blow and Garner, *Trans. Inst. Rubber Ind.*, 10, 465 (1935)) it was suggested that work on similar lines with rubber-carbon black stocks and rubber-softener mixtures might yield interesting results. The opportunity to carry out some experiments presented itself, and the results form the subject of this note.

Experimental.—A small Werner-Pfleiderer enclosed mixer, suitably modified to render it as gas-tight as possible, was employed. The weight of rubber taken for each test was 14 ounces. This was fed into the mixer piece by piece, over a period of two minutes, and milled for a further 5½ minutes; the atmosphere in the mixer was in one series nitrogen, freed from oxygen by passing through pyrogallol, and in another series oxygen. Sufficient gas was supplied to the mixer to maintain a pressure of about 5 cm. of water. The conditions of temperature, time, etc., were as accurately controlled as possible.

Plasticity measurements were made 30 hours after the milling process, the plasticity figure being the time in seconds taken to compress a pellet (1 sq. cm. in cross-section and 1 cm. long) between platens 1 sq. cm. cross-section from a thickness of 7.5 to a thickness of 5 mm. under a load of 1000 gms. at 100° C.

Plasticization of Smoked Sheet.—Experiments were carried out under the conditions described on a sample of smoked sheet, with and without the addition of 3 per cent of zinc laurate; the zinc laurate, a rubber softener, was put into the mixer with the smoked sheet. The plasticity results obtained were as follows:

	Initially	After 6 Min. in Nitrogen	After 6 Min. in Oxygen
Smoked sheet	750	77	10.7
Smoked sheet + 3 per cent zinc laurate	...	16.5	4.0

Before adequate comparison can be made it is preferable to convert plasticities into minutes of mastication time as was done in the case of softeners (Blow and Garner, *loc. cit.*). The plasticity-mastication time curve of smoked sheet in nitrogen is taken as the basis, and then the plasticity figures become, by conversion, relative equivalent times of mastication (in minutes) in nitrogen, as follows:

	0	6	42
Smoked sheet	...	28	115
Smoked sheet + 3 per cent zinc laurate	...	28	115

Hence the softening effects are:

Softening effect of	Oxygen	3% Zinc Laurate	Oxygen and 3% Zinc Laurate
On smoked sheet	42 - 6 = 36	28 - 6 = 22	115 - 6 = 109

Plasticization of Carbon-Black-Smoked-Sheet Mix.—A parallel series of experiments was carried out on a carbon black master batch (carbon black 1, smoked sheet 2, by weight) mixed on open rolls some months previous. In order to avoid

stalling of mixer it was found necessary in this case to warm the rubber for 20 to 30 minutes at 70° C. The plasticity results were as follows:

	Initially	After 6 Min. in Nitrogen	After 6 Min. in Oxygen
Carbon black M.B.	805	8.6	4.0
Carbon black M.B. + 3 per cent zinc laurate	...	4.9	1.7

These become when converted to equivalent times of milling:

	Initially	After 6 Min. in Nitrogen	After 6 Min. in Oxygen
Carbon black M.B.	0	6	13.5
Carbon black M.B. + 3 per cent zinc laurate	...	11	32

The softening effects were thus:

Softening effect of	Oxygen	3% Zinc Laurate	Oxygen + 3% Zinc Laurate
On carbon black M.B.	$13\frac{1}{2} - 6 = 7\frac{1}{2}$	$11 - 6 = 5$	$32 - 6 = 26$

Discussion.—In the first place, confirmation of the effect of oxygen found by Cotton has been obtained.

From the plasticity results recorded above, the fact emerges that smoked sheet and a carbon black master batch of equal initial plasticity are not of equal plasticity after mastication under controlled conditions, in either nitrogen or oxygen. The rate of softening of the smoked sheet is slower than that of the carbon black master batch.

When plasticities are converted into mastication times, the softening effect of oxygen on smoked sheet is found to be greater than on the carbon black master batch. That is to say, not only is the absolute but also the relative softening of the carbon black mixture after mastication in nitrogen greater than that of smoked sheet. Likewise the effect of the softener studied (zinc laurate) on the carbon black master batch is lower both in nitrogen and oxygen.

It is of interest to note that the effect of the softener and oxygen is not additive, a fact that leads to the conclusion that the softener is more effective in the presence of oxygen than nitrogen.

These results throw some light on the mechanism of softening rubber by mechanical milling. Several explanations of the enhanced softening by the softener in the presence of oxygen suggest themselves. The softener may aid the dispersion of oxygen, or the dispersion of oxidized rubber; alternatively, it may, by softening the rubber, render a larger surface available for oxidation; the rate of spread of the softener may be greater on oxidized rubber, or the adhesion of softener to oxidized rubber may be greater, all of which possibilities would explain the facts.

The results on the carbon black master batch are complicated by the following facts: absorbed gas would be present in the carbon black as the rubber was masticated in air, and the batch mixed in air. The increased rate of softening, even in nitrogen, may be due, therefore, either to mechanical breakdown, to the absorbed oxygen and the "oxidized" rubber acting autocatalytically, or to a combination of these causes.

Insufficient work has been done to enable a decision to be made between the possible explanations, but the results recorded appear to be of more than passing interest.

Rubber Solvents and Substances Which Lower the Viscosity of Rubber Cements

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Because of the importance of the concentration of a cement and its viscosity with respect to its tendency to "set," these two features were investigated in the laboratory of the Institute in connection with the development of self-curing cements.

Preliminary experiments showed that cements of 7 per cent concentration are excellent in so far as stability and the convenience of handling and application are concerned. But whereas this concentration gives cements of suitable viscosity from plasticized rubber, the problem was to develop cements for the use of the shoe industry from unmilled rubber, which gives cements of better quality.

It is well known that the viscosity of rubber solutions depends greatly on the preliminary mechanical treatment of the rubber, *i. e.*, for a given concentration a solution of unplasticized rubber has a far higher viscosity than that of a solution of plasticized rubber. This is well illustrated by a diagram showing the relation between the viscosity of a rubber solution and the duration of preliminary mechanical treatment of the rubber (Fig. 1).

Even with reduction of the concentration of an unplasticized rubber solution to 5 per cent, the resulting viscosity proved to be too high. Any further reduction of the concentration was impractical because of the resulting poorer quality of the cement. Therefore, on a basis of information in the literature that the viscosity of rubber solutions can be greatly reduced by the addition of small quantities of certain liquids (piperidine, alcohols, acetone, etc.), we used ethyl alcohol for the reduction of viscosity and obtained a 5 per cent cement from unmilled rubber with a suitable viscosity.

On the basis of these preliminary results, it was decided to include in the investigation a detailed study of the effect of various diluents and their proportions on the properties of rubber cements with the idea of selecting the most effective and suitable agents and conditions for technical needs.

Since the beginning of the rubber industry, many attempts have been made to discover cheap and good solvents of rubber. The work of various investigators was directed, on the one hand, toward a search for new solvents, and on the other hand toward the development of methods for the more effective use of solvents already known. In old patents of the nineteenth century there are many references to the possibility of greatly increasing the effectiveness of rubber solvents by the addition of small quantities of certain liquid substances, such as alcohols, esters, organic bases, aldehydes, ketones, etc.

- This information indicated a means for reducing the time required for dissolving rubber, decreasing the volumes of solvents, etc., and, therefore, attracted the attention of investigators from theoretical as well as practical viewpoints. A long series of published investigations devoted to this problem has since appeared.

Thomson¹ claimed that the addition of 5 per cent of absolute alcohol to carbon

disulfide makes it possible to dissolve larger proportions of rubber. Lascelle and Scott² observed the same effect on the addition of 5 per cent of eucalyptus oil to benzine. Frank and Masckwald,³ in recommending the use of mixtures of carbon disulfide and carbon tetrachloride with and without the addition of benzine, asserted that the addition of 5 per cent of alcohol considerably increased their solvent effect and decreased the solution viscosity.

Le Blanc and Kröger⁴ showed that the addition of methyl, ethyl, and amyl alcohols to benzine solutions of rubber greatly reduces their viscosities. The most effective agent is methyl alcohol, and the least effective amyl alcohol. In other words, it was demonstrated that liquids which cause the least swelling decrease the

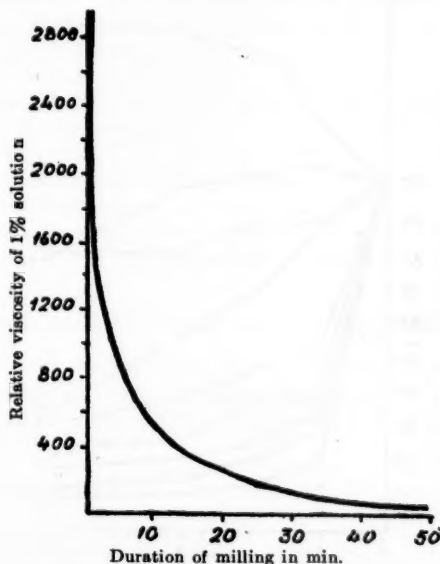


Figure 1—Relation between the Viscosity of Solution and the Duration of Milling of the Rubber

viscosity most. On the basis of these results, Le Blanc and Kröger assumed that the reduction of viscosity is the result of the desolvating action of these agents.

The same authors have also demonstrated a direct relation between the action of a solvent in reducing the viscosity of a rubber solution and the dielectric constant of the solvent, *i. e.*, at a given concentration the greater the dielectric constant of the solvent, the lower is the viscosity.

According to Whitby⁵ the viscosity of rubber solutions in anhydrous benzene is changed by the addition of organic acids or bases. Thus the addition of 0.4 mg. of piperidine to 100 cc. of solvent lowers the viscosity of a benzene solution of rubber by nearly 12 per cent.

Whitby and Jane⁶ have found that the addition of 0.1 per cent of a rubber solvent to a benzene solution of rubber has no marked influence on the viscosity, whereas the addition of 0.14 per cent of ethyl alcohol decreases the viscosity by 1 per cent.

Kawamura and Tanaka⁷ studied the effect of precipitants of rubber (acetone and alcohol) on the viscosity of rubber solutions in various solvents (carbon tetrachlo-

ride, benzine, acid, and chloroform) at different temperatures. Their results show that acetone and alcohol cause a lowering of viscosity, and with all the rubber solutions investigated, alcohol decreased the viscosity more than acetone. Their theory of the action of precipitants is based on the desolvating action of precipitants in a rubber solution, which increases with increasing concentration of the precipitant and decreases with increasing temperature. This conclusion of the authors is supported by the results of their experimental study.

From our viewpoint the work of Messenger and Porritt⁸ was of special interest. They made a detailed study of the reduction of viscosity of rubber solutions by the

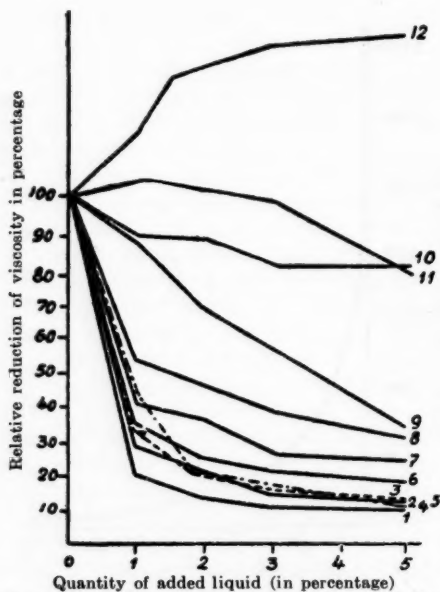


Figure 2—The Action of Different Liquids on the Viscosity of 5% Cement

- | | |
|------------------|-------------------|
| 1 Methyl alcohol | 7 Acetophenol |
| 2 Isomyl " | 8 Pyridine |
| 3 Propyl " | 9 Acetone |
| 4 Ethyl " | 10 Ethyleneglycol |
| 5 Butyl " | 11 Dichloroethane |
| 6 Isopropyl " | 12 Water |

addition of various liquids and showed the action of the latter in relation to numerous factors. The general conclusions from the results of their investigation are as follows:

1. Solutions of rubber of any concentration are less viscous when prepared with the addition of certain liquids to the solvent than with the use of pure solvents.
2. Rubber solvents (carbon disulfide, carbon tetrachloride, etc.) do not lower the viscosity of rubber solutions; this ability is possessed by certain non-solvents containing oxygen in their molecules, including alcohols, aldehydes, ketones, esters, and water.

Of the non-solvents investigated, the ability to reduce viscosity increases in the following order: butyraldehyde, acetone, ethanol, methanol, *i. e.*, the effect in-

creases with decrease in the solvent power for raw rubber, in the swelling power for vulcanized rubber, and with increase in the dielectric constant.

3. With increasing concentration of active liquid, the viscosity decreases at a gradually decreasing rate. The main practical effect is obtained by the addition of the first 2-3 per cent of alcohol.

4. The more viscous the original solution, and the less the rubber has been previously milled, the more the viscosity is reduced by an active liquid.

Somewhat contradictory are the views of various investigators of the effect of water on the viscosity of rubber solutions. de Vries⁹ has shown that on the addition of water to a benzene-rubber solution the viscosity slightly increases. van Rossem¹⁰ has also observed that anhydrous benzene gives a less viscous solution than benzene containing moisture. According to the data of Messenger and Porritt,⁸ the addition of water within the limits of its solubility to a rubber solution results in a slight reduction of the viscosity. These authors suppose that the disagreement of various investigators in judging the action of water probably depends on the various moisture contents already present in the solvents and in the rubber, and point out that in studies of the viscosity particular attention must be given to the moisture contents of the ingredients in a rubber solution.

This work is of practical interest in connection with problems of industrial production, and therefore the experiments in the present work were carried out with commercial materials without any preliminary purification or drying.

Methods of Preparation of Cement and Determination of Its Viscosity

"Galosh" benzene and smoked sheet rubber were used as raw materials. The rubber was not plasticized, but to facilitate dissolving, it was passed three times through tightly fitting mill rolls. After a sample was treated in this manner, it was

TABLE I. VISCOSITY CALCD. IN PERCENTAGE OF THE CONTROL CEMENT VISCOSITY

Concentration of Added Liquid (in Grams) per 100 Grams of Cement	Methyl Alcohol	Isoamyl Alcohol	Propyl Alcohol	Ethyl Alcohol	Isopropyl Alcohol	Butyl Alcohol	Acetophenol	Pyridine	Acetone	Ethylene Glycol (Imported)	Dichloroethane	Water
0	100	100	100	100	100	100	100	100	100	100	100	100
1	20.1	29.1	33.4	45.4	35.2	38.9	41.6	53.4	87.6	88	105	118
2	14.2	21	19.8	20.9	25.7	26	35.6	45.8	68.2	87	92.6	135
3	11.3	14.9	15.8	16.3	21.9	18.1	27	38.6	56.7	80	98.8	145
5	10.2	12.6	13	12.3	18	12.7	23.7	30.2	33.4	80	78.7	146

placed in a half portion of the solvent for swelling; after 24 hours of swelling the remaining half of the solvent was added, and the solution was agitated in a shaking machine for 12-15 hours to complete homogeneity. The prepared cement was divided into 150-gram units and placed in special jars of white glass. The active liquid to be tested was introduced slowly and with constant stirring into the cement. After it had stood for 1 hour at room temperature, the viscosity was determined in a Stormer viscometer with a falling weight of 200 grams at 25° C. The results were expressed by the elapsed time (in seconds) required for 100 revolutions of the viscometer cylinder.

The Action of Various Liquids on the Viscosity of Solutions

The following liquids were tested: water, rubber solvents (dichloroethane, pyridine), non-solvents of rubber (methyl, ethyl, isoamyl, propyl, isopropyl, and butyl alcohols; acetophenol, acetone, ethyleneglycol). In each case 1 to 5 per cent was added to the cement.

The viscosity determinations are shown in Tables I and II. The viscosity of the control cement in benzine was assigned the value 100, and the viscosities of all other cements were calculated as percentages of the viscosity of the control cement.

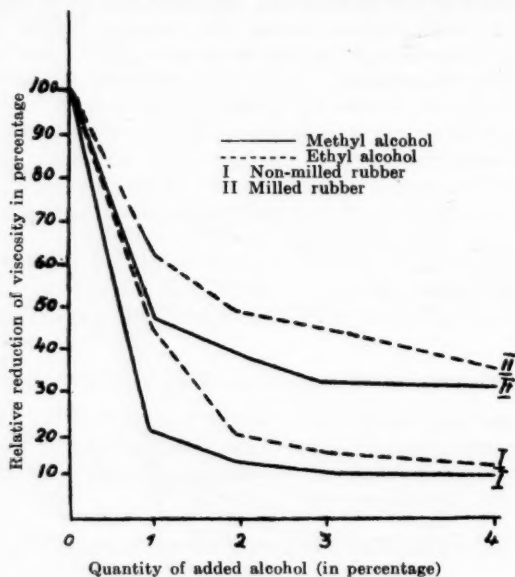


Figure 3—The Effect of Milling on the Action of Ethyl and Methyl Alcohols

It can be seen from Tables I and II that the greatest reductions in viscosity were produced by alcohols, and of these methyl alcohol is the most suitable. Acetophenol, pyridine, and acetone are considerably less effective than alcohols. Ethyleneglycol and dichloroethane reduce the viscosity but very little. The addition of water within the limits of 1 to 5 per cent increased considerably the viscosity.

TABLE II. VISCOSITY CALCD. IN PERCENTAGE OF THE CONTROL CEMENT VISCOSITY

Concentration of Alcohol (in Grams per 100 Grams of Cement)	Methyl Alcohol		Ethyl Alcohol	
	Non-Milled Rubber	Milled Rubber	Non-Milled Rubber	Milled Rubber
0	100	100	100	100
1	20.1	47.2	45.4	63
2	14.2	38.8	20.9	48.2
3	11.3	32	16.3	44.5
5	10.2	30.5	12.3	34.6

The extent to which the viscosity diminished increased with increasing concentration of active liquid. Addition of an alcohol up to 3 per cent reduced abruptly the viscosity. On further addition of alcohol the reduction of viscosity became progressively less, and practically ceased with more than 3 per cent of an alcohol.

The Action of Preliminary Milling of Rubber on the Effects Produced by Methyl and Ethyl Alcohols

In view of the results shown in Fig. 1, the study of viscosity was continued with the methyl and ethyl alcohols alone.

To investigate the effect of plasticization of rubber on the degree of viscosity reduction by alcohols, 5 per cent solutions were prepared from unmilled rubber and

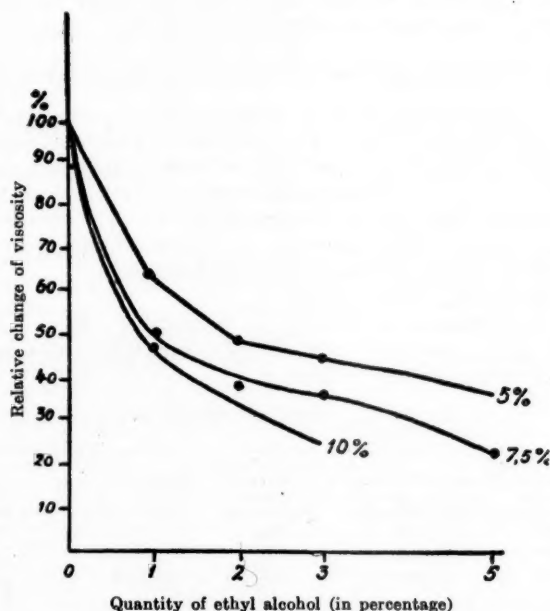


Figure 4—The Action of Ethyl Alcohol in Relation to the Concentration of Cement

from rubber plasticized on a laboratory mill for 5 minutes with a roll temperature of 55–60° C. The initial viscosities and the viscosities after the addition of 1 to 5 per cent (of the weight of cement) of methyl and ethyl alcohols were then determined. The viscosities of each of the cements, calculated as percentages of the viscosity of the control cement, are shown in Tables I and II.

The reduction of viscosity by methyl and ethyl alcohols is much greater for the cements prepared from plasticized rubber than for the cements from unplasticized rubber.

The Effect of Ethyl Alcohol on the Viscosity in Relation to the Concentration of Cement

To determine the effect of ethyl alcohol on viscosity in relation to the concentration of a cement, 5, 7.5, and 10 per cent solutions of milled rubber were prepared.

The results of viscosity measurements of these solutions after addition of 1 to 5 per cent of ethyl alcohol, calculated as percentages of the viscosity of the control cement taken as 100, are shown in Table III and Fig. 4.

TABLE III. CONCENTRATION OF CEMENT

Concentration of Alcohol (in Grams per 100 Grams of Cement)	5%	7.5%	10%
0	100	100	100
1	63	50.3	49
2	48.2	38.5	...
3	44.5	35.9	24.8
5	34.6	21.2	...

It can be seen from Table III and Fig. 4 that the higher the concentration of cement the greater is the reduction of viscosity by alcohol.

The Effect of Ethyl Alcohol on the Viscosity in Preservation of Cement

With a view to ascertaining the effect of ethyl alcohol on cements during storage, the following test was carried out. Two solutions of 5 per cent cement were prepared from milled and unmilled rubber, as in the study of the effect of plasticization. To the freshly prepared cements was added 3 per cent of ethyl alcohol, and the mixtures were stored for some time in darkness at 20° C. The viscosities were measured at definite periods. The viscosities of cements containing no ethyl alcohol, and stored under the same conditions, were also determined.

The results are shown in Tables IV and V.

Regardless of the presence of alcohol, the viscosity of cement increased during storage. It should be noted that on prolonged storage the increase in viscosity was relatively greater in the presence of alcohol.

TABLE IV. UNPLASTICIZED RUBBER

Storage Duration (in Hrs.)	Cement Containing No Ethyl Alcohol		Cement Containing 3% Ethyl Alcohol	
	Cement Viscosity (in Sec. per 100 Revolutions)	Relative Change of Viscosity	Cement Viscosity (in Sec. per 100 Revolutions)	Relative Change of Viscosity
0	2160	100	211	100
24	3193	148	271	128
240	4240	197	674	315

TABLE V. PLASTICIZED RUBBER

Storage Duration of Cement (in Hrs.)	Cement Containing No Ethyl Alcohol		Cement Containing 3% Ethyl Alcohol	
	Viscosity (in Sec. per 100 Revolutions)	Change of Viscosity (in %)	Viscosity (in Sec. per 100 Revolutions)	Change of Viscosity (in %)
0	91.2	100	40.6	100
120	95	104	47	113

Gelation of Self-Curing Cements in the Presence of Methyl and Ethyl Alcohols

Since the object of this work was the application of substances which reduce the viscosity of self-curing cements, the effect of these active materials (particularly that of ethyl and ethyl alcohols) on the rate of gelation of a 5 per cent cement in benzene was investigated.

A self-curing cement of the following composition was tested (in parts by weight):

Smoked sheet	100
Zinc oxide	5
Sulfur	3
Zinc butylxanthate	3
<i>p</i> -toluidine	1

A 5 per cent solution of unplasticized rubber was prepared in the usual manner, and the ingredients were introduced in the following way: *p*-toluidine was added directly; the other ingredients were mixed with a small portion of the cement and the resulting paste was added to the main portion. One part of cement was mixed with 3 per cent of ethyl alcohol and another with 2 per cent of methyl alcohol (the different quantities of alcohols were used to obtain a close initial viscosity of cement).

The cements were stored in darkness at 20–25° C. with periodical measurements of their viscosities until the point of incipient gelation.

The results of these experiments are given in Table VI.

TABLE VI. DURATION OF STORAGE OF CEMENTS (IN HRS.)

Introduced Alcohols	1	3	6	12	24	48
Ethyl	405	470	606	804	25420	Gel
Methyl	560	821	828	1556	Gel	...

Table VI shows that methyl alcohol causes gelation more rapidly than ethyl alcohol. Moreover in general methyl alcohol, in distinction to ethyl alcohol, in addition to its ability to reduce the viscosity of freshly prepared cement, also increases the viscosity of cements during storage.

Table VII gives the viscosity changes during storage of solutions of plasticized rubber containing alcohols.

TABLE VII. DURATION OF THE STORAGE OF SOLUTION

Alcohol Concentration (in Grams per 100 Grams of Cement)	Ethyl Alcohol			Methyl Alcohol		
	Initial Viscosity	5 days	10 days	Initial Viscosity	5 days	10 days
0	91.2	95	...	91.2	95	...
1	58.4	66	69	43	52	60
2	44	50	46	35.4	37	61
3	40.6	47	51	29.2	57	76
5	31.6	32.3	..	27.8	76	122

A comparison of the results of our observations with the general conclusions of Messenger and Porritt reveals a nearly complete analogy in spite of the fact that the methods of investigation and the materials used were different.

Conclusions

1. The greatest effect in reducing the viscosity of rubber solutions is produced by alcohols. This effectiveness increases in the following order: isopropyl, butyl, ethyl propyl, isoamyl, and methyl alcohol. Of these the most active is methyl alcohol and the least active isopropyl alcohol; all other alcohols are closely similar in action. Acetophenol, pyridine, and acetone also reduce considerably the viscosity of rubber solutions, but are greatly inferior in their effectiveness to the alcohols. Ethyleneglycol and dichloroethane reduce the viscosity very little.

The addition of 1 to 5 per cent of water greatly increases the viscosity, which

contradicts the observations of Messenger and Porritt.⁸ However the concentration of water in our experiments was considerably higher than that used by these authors.

2. With higher concentrations of active liquids, the degree of reduction of viscosity increases, but there is a definite limit of concentration above which further reduction of viscosity is very small. With alcohols this limiting concentration is at 2-3 per cent.

3. The effect of active substances in the reduction of viscosity depends on the concentration of the cement and on the preliminary mechanical treatment of the rubber, *i. e.*, the greater the concentration of cement and the less the rubber is subjected to preliminary mechanical treatment, the greater the reduction of the viscosity; in other words the higher the original viscosity the greater is the reduction in the viscosity by active substances.

4. The viscosity of a rubber cement increases during storage, regardless of the presence of an alcohol. During short periods of storage (up to 1 day) the effectiveness of the alcohol is maintained, but during prolonged storage its action decreases and with methyl alcohol the viscosity actually increases.

5. The rate of gelation of a self-curing cement depends on the nature of the viscosity-reducing agent. Methyl alcohol causes more rapid gelation than ethyl alcohol.

In conclusion, for reducing the viscosity of self-curing cements the addition of 3 parts of ethyl alcohol to 100 parts by weight of a cement is recommended as the best procedure for industrial requirements.

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The Effect of Addition of Colloids on the Coagulation of Latex

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1. Introduction

There have been many investigations concerned with the coagulation of latex. de Vries and Beumée-Nieuwland (*Arch. Rubbercultuur*, 11, 497 (1927); 12, 441 (1928); 12, 454 (1928); 13, 125 (1929)) described the behavior of sodium chloride, alum, alcohol, borax, caustic soda, ammonia, sodium phosphate, and the salts of heavy metals as coagulants (or anticoagulants) of latex.

Whitby (*Kolloid Z.*, 12, 147 (1913)) studied the natural and acid coagulation of Hevea latex, and found that coagulation was complete with a certain definite proportion of acid, whereas coagulation was incomplete when this proportion was exceeded; still further addition of acid, however, caused renewed coagulation. A similar result was obtained with sulfuric acid instead of hydrochloric acid, but here there was no incomplete coagulation; above a certain proportion, acetic acid caused incomplete coagulation and there was no second coagulation when it was increased further. The results were expressed by plotting the amount of acid added as abscissae and the state of coagulation as ordinates.

Van Harpen (*Arch. Rubbercultuur*, 15, 1 (1931)) estimated the p_H value of Hevea latex, and Fullerton (*Quart. J. Rubber Res. Inst. Malaya*, 2, 156 (1931)) studied the relation of the p_H value and the coagulation of latex, and found that coagulation started at p_H 5.30 and was complete at p_H 4.87 or below.

Rapid progress has recently been made in the use of latex and a large amount of concentrated latex is now produced. There are moreover numerous patents for anticoagulants of latex. Anticoagulants include nearly all colloidal substances, but unfortunately there has been no report on studies of this subject. Accordingly the authors undertook experiments to obtain a fundamental knowledge in this field.

2. Latex Samples and Methods of Experimentation

The latex was supplied by Sanwa Co., and the analysis of two samples gave the following results:

	Sample A	Sample B
Total solids	38.2%	38.3%
Rubber	35.3%	35.5%
Ammonia(grams of NH_3 per liter)	7	3.7

Since this ammoniated latex contained too much rubber and was unsuitable for experimental purposes because the alkalinity due to ammonia caused large experimental errors, the ammonia was removed by dialysis; the latex was then diluted so as to contain 3.5 per cent rubber. The latex was dialyzed by suspending a parchment sac in the latex and allowing water to flow into the sac until the latex was neutral to litmus. This required 2 to 3 days.

In the coagulation of latex, a coagulated mass and a clear serum are formed from a complete emulsion through various intermediate stages. To observe these

changes in detail, the authors followed the changes in external appearance as described by Whitby (*loc. cit.*), since the changes in viscosity were not only difficult to measure but the results were inaccurate because of the viscosity of the serum.

To 50 g. portions of latex (≈ 10 mg.) in Erlenmeyer flasks were added 0.2 *N* (or 1 *N*) acids in different proportions (0.1 cc. or 0.2 cc. at a time), and the state of coagulation and the separation of serum were determined after standing for 24 hours. When studying the effect of colloids, the latter were added before the acid, and the condition was examined after standing for 24 hours.

Though the procedure seems inaccurate, it supplied sufficient data to show the relation between the coagulation of latex and the proportion of acid to be added, since there were appreciable differences in the state of coagulation by a change of 0.1 cc. of acid.

For the change of latex from a complete emulsion to a separation of clear serum, the authors classified five stages:

1. Perfect emulsion. A homogeneous, milky appearance, as the latex samples.
2. Partial flocculation. A separation of serum at the bottom, but an apparently complete dispersion by agitation.
3. Complete flocculation. A separation of serum at the bottom as in stage 2, but a change to small granules or flocculates on shaking.
4. Incomplete coagulation. An external appearance similar to that of stage 3, but larger granules and an easily distinguishable mass of coagulated rubber.
5. Complete coagulation. Serum separated and the coagulated masses united into one large mass which cannot be broken into smaller granules by agitation.

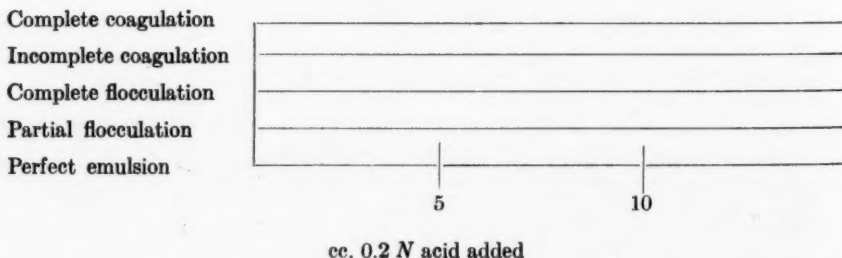
The relation between the coagulation of latex and the proportion of acid can be expressed in curves by arranging these five stages of coagulation as ordinate and the proportion of acid as abscissa. All the values are based on 50 grams of dialyzed, diluted latex containing 3.5 per cent rubber and 0.2 *N* acid (with 1 *N* acid, the calculations are converted to the amounts of 0.2 *N* acid).

3. Coagulation Curves of Latex with Acetic, Hydrochloric, Sulfuric, and Nitric Acids

The coagulation curves of dialyzed latex with acetic, hydrochloric, sulfuric, and nitric acids are shown in Figs. 1 to 4.

These curves indicate that latex is completely coagulated by a small proportion of acid, disperses completely again on exceeding this limit, and coagulates again by further addition of acid, *i. e.*, there is a first and a second period of coagulation in the coagulation curve, and there is an acid dispersion between the first and second period, so that the latex is a comparatively stable emulsion within a certain limit of acidity. Another noteworthy fact is that the complete coagulation of latex is irre-

EXPLANATION OF FIGURES



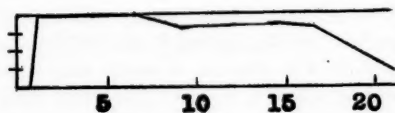


Fig. 1. Acetic acid

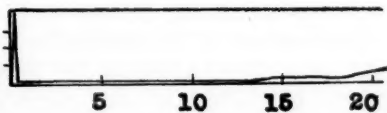


Fig. 2. Hydrochloric acid

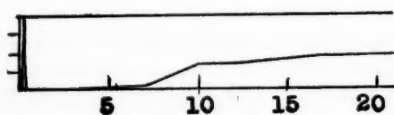


Fig. 3. Sulfuric acid

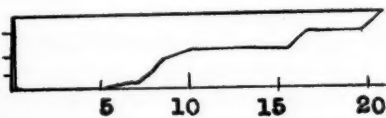
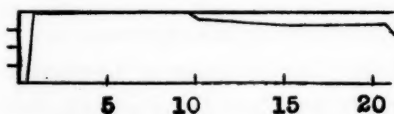
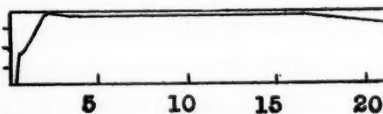
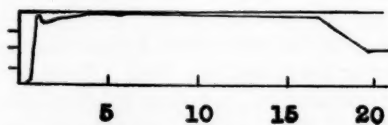
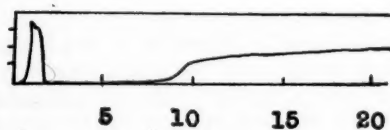
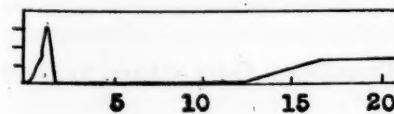
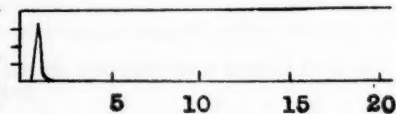


Fig. 4. Nitric acid

Fig. 5. Gum arabic
(0.042%)Fig. 6. Gum arabic
(0.14%)Fig. 7. Gum arabic
(0.57%)Fig. 8. Gum arabic
(1.71%)Fig. 9. Gum arabic
(2.83%)Fig. 10. Gum arabic
(5.67%)

versible and those samples which were completely coagulated at the first period could not be dispersed again by more acid. Accordingly, it is safer to add the acid from a burette and then stir than to add small amounts of acid slowly with agitation.

A comparison of the coagulation curves of acetic, hydrochloric, sulfuric, and nitric acids indicates that the first coagulation with the use of acetic acid extends over a considerable range, and then gradually turns to an acid dispersion with an increase of acid. With hydrochloric, sulfuric, and nitric acids, the first coagulations extended over only small ranges, and further additions of acids formed complete emulsions. The curves at this stage show nearly identical tendencies with all three mineral acids, in contrast to the curve of acetic acid. It is therefore considered that the coagulation depends chiefly on the hydrogen-ion concentration, as reported by various investigators.

The negatively charged rubber particles stop their Brownian movement at a definite hydrogen-ion concentration and reach complete coagulation; the hydrogen-ion concentration at this stage has a close relation to the isoelectric point of the protein which is adsorbed on the surface of rubber particles and acts as a protective colloid.

Rubber particles dispersed in an acid medium are not very sensitive to the hydrogen-ion concentration of the dispersed medium. This may be due to the adsorption of hydrogen ions on the surface of rubber particles, so that the charge of the particles becomes opposite to that of particles dispersed in a neutral or alkaline medium. One proof of such a view is that the curves at the second stage of coagulation are different because of the difference in the anions of the acid, and the coagulation at this stage seems to be affected by the anions rather than by hydrogen ions.

4. Effect of Gum Arabic on the Coagulation Curve of Latex by Acetic Acid

Gum arabic amounting to 0.042, 0.14, 0.57, 1.71, 2.83, and 5.67 per cent (based on the rubber contained in latex) was added to latex and the latex then coagulated with acetic acid. The coagulation curves with 0.2 *N* acetic acid are shown in Figs. 5, 6, 7, 8, 9, and 10.

When the proportion of gum arabic was small, *i. e.*, with 0.042–0.57 per cent, it required more acid for coagulation than without gum arabic, and the range of the first coagulation became greater, so that it required a comparatively large amount of acid to reach a dispersion in acid medium. On the other hand, coagulation became incomplete and the serum showed more or less turbidity. With 1.71 per cent of gum arabic, the form of the curve changed considerably, the first coagulation in the curve had only a short range and the dispersion in acid medium appeared soon, had only a short duration, and then passed to the second stage of coagulation. With an increase in the gum arabic the first coagulation became still more incomplete, and the second coagulation was only partial and is hardly recognizable on the curve.

This test on ammoniated latex indicates that gum arabic has little effect as a protective colloid or that the protection is very weak compared with dialyzed latex. This difference may be due to an inefficient adsorption between gum arabic and rubber particles when the rubber particles hold ammonia adsorbed on the surface.

5. Effect of Casein and Saponin on the Coagulation Curve of Latex by Acetic Acid

Since casein is insoluble in water, it was dissolved in aqueous caustic potash of definite concentration. In order to test the effect of the caustic potash-casein solution, caustic potash alone of the same concentration was added to the latex; the coagulation curve indicates that caustic potash has no marked influence except that it requires more time and more acetic acid to give the first coagulation.

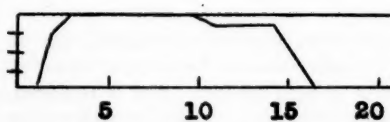


Fig. 11. Casein
(0.57%)

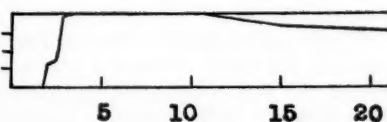


Fig. 12. Casein
(2.12%)

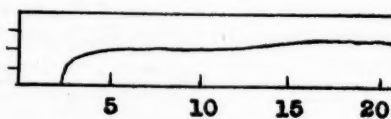


Fig. 13. Casein
(2.83%)

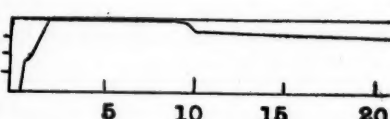


Fig. 14. Saponin
(0.14%)

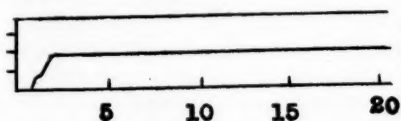


Fig. 15. Saponin
(0.71%)

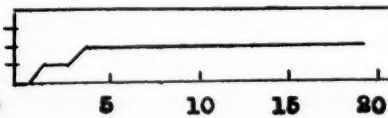


Fig. 16. Saponin
(2.83%)

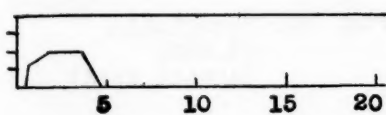


Fig. 17. Gum traganth
(0.71%)

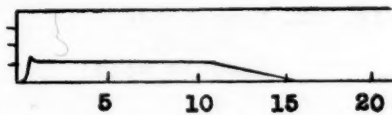


Fig. 18. Gum traganth
(1.42%)

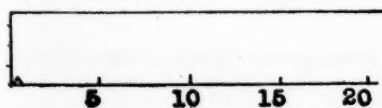


Fig. 19. Gum traganth
(2.83%)

The coagulation curves of latex with 0.57, 2.12, and 2.83% casein are shown in Figs. 11, 12, and 13 and those of 0.14, 0.71, and 2.83 per cent saponin in Figs. 14, 15, and 16.

Casein and saponin have similar actions as protective colloids, except that saponin has more protective power than does casein. Both had a tendency to retard the first coagulation and dispersion in acid medium, and it required more time in each of these periods. An increased proportion caused in each case a state of coagulation which passed beyond the flocculation stage only with difficulty.

6. Effect of Gum Tragacanth on the Coagulation of Latex by Hydrochloric Acid

Since gum tragacanth has greater power as a protective colloid, an experiment was carried out using 0.2 *N* acid. The results with 0.71, 1.42, and 2.83 per cent gum tragacanth based on the rubber in the latex are shown in Figs. 17, 18, and 19.

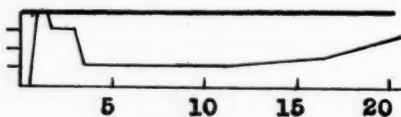


Fig. 20. Funori (HCl)
(0.28%)

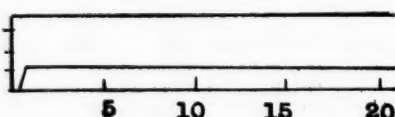


Fig. 21. Funori (HCl)
(1.91%)

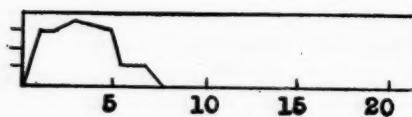


Fig. 22. Hemoglobin
(0.57%)
(Acetic acid)

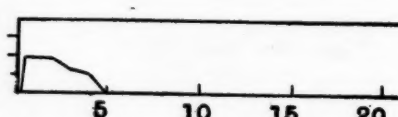


Fig. 23. Hemoglobin
(2.83%)
(Acetic acid)

Gum tragacanth was prepared by soaking in water for one week, then boiling and cooling; the coagulation curves were then obtained by adding hydrochloric acid. Gum tragacanth showed a greater efficiency of anticoagulation, but this efficiency was not obtained by the simple addition of unheated gum arabic solution to latex, perhaps because of inefficient adsorption between the particles of latex and gum tragacanth.

7. Effect of Dextrin, Glue, "Funori," Hemoglobin, Turkey-red Oil, and Lecithin

The effects of dextrin, glue, "funori" (a sea-weed preparation), hemoglobin, Turkey-red oil, and lecithin were also studied by the same method.

Dextrin had no influence on the coagulation of latex while glue had some action as a protective colloid in large quantity, but it had no influence when the concentration was below 0.29%.

"Funori" had a tendency to give a prolonged first coagulation period, and it

hastened the second coagulation so that it acted as a coagulation accelerator when the concentration was around 0.28 per cent, but above 1.91 per cent it gave a curve similar to that of gum tragacanth. The results are shown in Figs. 20 and 21.

Hemoglobin was an efficient protective colloid, and an addition of 0.57 per cent completely prevented coagulation with acetic acid. The results are shown in Figs. 22 and 23.

Since Turkey-red oil has the property of neutralizing strong acids, it gave a relatively long first coagulation period, a hard and compact mass and a clear serum, so that the action resembled that of a coagulation accelerator.

The addition of lecithin in dilute alkali to latex prolonged the first coagulation period, and it acted as a coagulation accelerator.

8. Summary

1. A known proportion of colloid was added to dilute, dialyzed latex (rubber content 3.5 per cent) to determine the effect of colloids on the coagulation of latex. Various proportions of 0.2 *N* acids were added; the mixtures were then left for 24 hours. The relations between the state of coagulation of latex and the proportion of acid are shown graphically.

2. The coagulation curves of acetic, hydrochloric, sulfuric, and nitric acids show that latex is coagulated by a definite quantity of acid, above which proportion the coagulation disappears and then reappears by further addition of acid. The first coagulation is apparently governed by the p_H value of the dispersed medium, and the charge on the surface of the rubber particles is opposite to that of rubber dispersed in an alkaline medium. The second coagulation is governed by the concentration of cations.

3. Gum arabic, casein, saponin, gum tragacanth, glue, "funori," or hemoglobin were added to latex and coagulation obtained by the addition of 0.2 *N* acetic acid or hydrochloric acid. Each gave the characteristic curve of a protective colloid; dextrin, however, had no influence on the coagulation curve.

4. The influence of the colloids on the coagulation curve is of particular interest in studying further the properties of colloids and rubber particles, and this will be discussed in detail in connection with further investigations.

The Internal Heating of Ebonite during Vulcanization

H. A. Daynes

It is known that the reaction between rubber and sulfur to form ebonite is strongly exothermic, and under certain conditions may cause a marked internal rise of temperature during vulcanization. This heating is sufficient in many cases to accelerate the rate of vulcanization of the center of the mass to an important extent, so that the degree of vulcanization of the center differs from that of the surface, the product thus being non-uniform in physical properties. In more severe cases the temperature may rise sufficiently to cause decomposition, evolution of gas and porosity, or even violent explosion. This internal heating is favored by a high temperature of vulcanization, by great thickness of the mass to be vulcanized, by the addition of accelerators of vulcanization, and by the omission from the mixing of inert compounding ingredients, which act as diluents. It is, perhaps, not so commonly known that the heating is greater in an open steam cure, owing to the lower rate of dissipation of heat from the surface, though this factor may have been one of those leading to the common adoption of the water immersion method of cure. In technical practice the inconvenience of this phenomenon is avoided as far as possible by a control of the factors mentioned, including such devices as the inclusion of semi-vulcanized ebonite dust or crumb, building-up from semi-vulcanized sheets, "stepped" or rising cures, or, where possible, by designing the object so as to facilitate conduction of heat from the center by means of recesses or metal inserts.

The nature of the effect has been made clear by a number of experimental investigations in which embedded thermocouples were used to compare the temperature conditions during vulcanization with those of a similar mass in which vulcanization was already complete (Toyobe, *J. Soc. Chem. Ind., Japan*, 33, 96B, 275B (1930); Riding, *Trans. Inst. Rubber Ind.*, 6, 230 (1931); Hada and Nakajima, *J. Rubber Soc., Japan*, 5, 288 (1932); Blake, *Ind. Eng. Chem.*, 26, 1283 (1934)). The mathematical theory of these temperature changes is very complicated, and to judge from published literature, little progress seems to have been made towards its solution. For example, it is usually assumed, without justification, that the point at which the internal temperature reaches a maximum during vulcanization is necessarily that at which the rate of production of heat is at a maximum. It may, therefore, help to clarify ideas on the subject if an approximate representation of a simplified case is considered.

Simple Theory

It is clear that the dissipation of heat by conduction is an essential factor in every case, as the heat of vulcanization (about 300 cal. per g.) and specific heat (about 0.33) are such that if no heat were lost by conduction or decomposition the temperature of the mass would be raised about 1000° C.

Consider a composite sheet (Fig. 1) made up of a thin layer of unvulcanized ebonite stock between two equal layers of a material of the same thermal conductivity as the ebonite, but not subject to any chemical reaction on heating. The thickness of the internal layer is supposed to be a constant fraction f of the com-

bined thickness $2d$ of the outer layers. It is assumed also that the center layer is thin enough for its temperature to be practically uniform.

Consider a portion of the sheet of 1 sq. cm. area.

Let K = thermal conductivity of the material.

θ = temperature of center layer in $^{\circ}\text{C}$.

ϕ = surface temperature in $^{\circ}\text{C}$, i. e., temperature of vulcanization as determined by the platens of the press, for example.

R_{θ} = rate of production of heat in calories per second per cubic centimeter of unvulcanized stock at a temperature θ .

a = temperature coefficient of reaction, i. e.,

$$\frac{R_{\theta}}{R_{100}} = a^{\frac{\theta-100}{10}};$$

100°C . being taken arbitrarily as a convenient basis of reference.

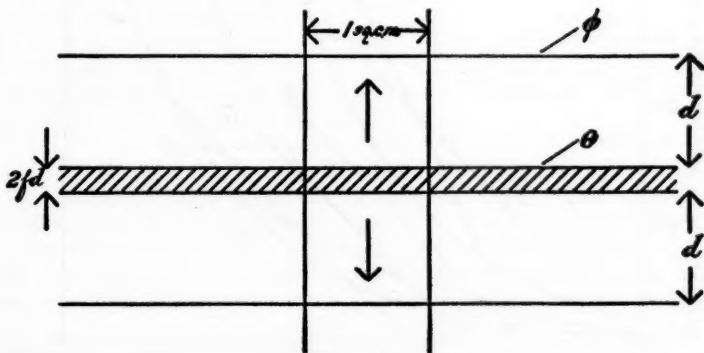


Figure 1

Then, heat produced per sec. per sq. cm. of sheet

$$H_1 = 2fd R_{\theta} = 2fd R_{100} a^{\frac{\theta-100}{10}}.$$

Next consider the loss of heat by conduction if the rate of production of heat were to be maintained constant sufficiently long for the attainment of equilibrium.

The total rate of heat loss in both directions

$$H_2 = \frac{2K}{d} (\theta - \phi).$$

Under equilibrium conditions $H_1 = H_2$, so that

$$\frac{(\theta - \phi)}{a^{\frac{\theta-100}{10}}} = \frac{fd^2 R_{100}}{K}.$$

There is no simple algebraical solution to this equation, but the results may be understood from the graphs of Fig. 2. It is seen from the equation that the rise of temperature varies as the reactivity R_{100} , as a function of temperature which increases with temperature, as the square of thickness, and inversely as the thermal conductivity.

The curve b , ($H_1 = 2fdR\theta$), is calculated assuming a value 2.5 for the temperature coefficient a , but the exact value is comparatively unimportant for the present purpose. The ordinates represent rate of heat production and the abscissae the temperature θ of the central layer of ebonite. The straight line B , [$H_2 = \frac{2K}{d}(\theta - \phi)$], represents the relation between the rate of heat loss and the temperature θ . The equilibrium temperature θ^1 is given by the first point of intersection of b and B , and the rise of temperature by the horizontal distance $\theta^1 - \phi$, ϕ being the vulcanizing temperature. If there were no intersection the system would be thermally unstable

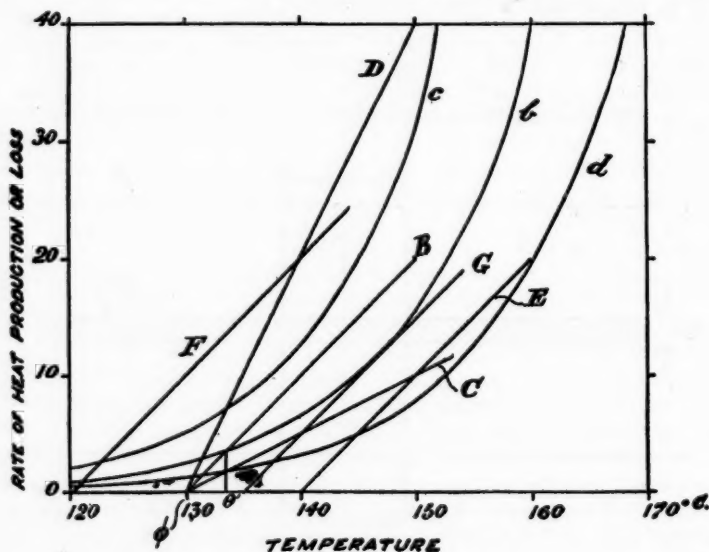


Figure 2

and porosity or explosion would occur. If B were tangential to b the system would be just stable and a rise of temperature of about 11°C . ($= \frac{10}{\log_e a}$) would occur.

(As this figure is not directly applicable to practical cases the proof is not given here.) The case shown has been chosen arbitrarily and shows equilibrium with a rise of 3.5°C . The effects of varying the controllable factors R_{100} , K , d , and ϕ are shown by the following additional lines and curves: Curves c and d are similar in shape to b , but with the ordinates doubled and halved, respectively. Lines C and D have the same intercept on the temperature axis as B but with the slope halved and doubled, respectively. Lines E and F have the same slope as B but are displaced from B along the temperature axis by $+10^\circ\text{C}$. and -10°C ., respectively. G has the same slope as B but is tangential to b .

Now consider the effects of varying the factors R_{100} , K , d , and ϕ .

1. *Reactivity R_{100} of Stock.*—The main effect of altering the mixing is to change the curve b in the direction of c or d .

- (i) If the mixing is diluted with inert fillers or dust until the reactivity is halved, the rise of temperature, as shown by the point of intersection of B and d , is reduced from 3.5°C . to 1.5°C .

- (ii) If the reactivity is doubled by omitting inert ingredients or adding accelerators, as shown by curve *c*, there is no intersection with *B* and the system is unstable.

In the practical case, however, changing the mixing may also affect the thermal conductivity and so alter the slope of *B*.

2. *Thermal Conductivity K of Outer Layers*.—The effect of altering the thermal conductivity is to change the slope of *B* in the direction of *C* or *D*.

- (i) If the conductivity is halved by the substitution of one ingredient for another, as shown by line *C*, there is no intersection and the system is unstable.
- (ii) If the conductivity is doubled, as shown by line *D*, the temperature rise is reduced to about 1.5° C.

Changing the mixing may also alter the reactivity and so alter curve *b*.

3. *Thickness d of the Sheet*.—The effect of altering the thickness of the sheet is to alter the slope of line *B* and also to change curve *b* since the volume of the vulcanizing layer is changed.

- (i) If the thickness is halved, as shown by curve *d* and line *D*, the temperature rise is much reduced to about 0.7° C.
- (ii) If the thickness is doubled as shown by curve *c* and line *C*, the system is very unstable.

4. *Vulcanization Temperature ϕ* .—The effect of altering the vulcanization temperature is to displace *B* to the right or left.

- (i) If the vulcanization temperature is reduced by 10° C., as shown by line *F*, the temperature rise is reduced to about 1° C.
- (ii) If the vulcanization temperature is increased by 10° C., as shown by line *E*, the system is unstable. One condition in which the system is just stable is shown by curve *b* and line *G*, the temperature rise being 11° C.

In all these cases it will be seen that the margin between instability and a temperature rise of 3.5° C. is small, especially in the case of a change in thickness.

Complicating Factors Preventing Quantitative Application of This Theory to Practical Cases

This simple case differs from the practical case of, say, the vulcanization of a sheet of ebonite, so that it cannot be applied quantitatively, though it is useful for visualizing qualitatively the effects of various factors. Some of the complicating factors which have been ignored will now be briefly indicated.

(a) The reactivity R_{100} has been treated as if it were a constant property of the mixing. In fact, it varies during vulcanization according to the degree of combination of the rubber and sulfur. Observations of its variation have been made by various workers, but briefly it may be said that the rate of heat production is small or perhaps negative during the early stages, while soft rubber is being formed, and then rises, passing through a maximum, and returns to zero when chemical combination is complete. The relation between heat production and percentage of combined sulfur has not yet been expressed in any simple mathematical form which lends itself to calculation.

(b) It has been assumed that equilibrium is reached between the heat produced by the reaction and that lost by conduction. In fact, owing to the heat capacity of the material, some of the heat produced is used in raising the temperature of the mass. Consequently the maximum temperature tends to be lower and to occur after the point of maximum reactivity is past; further, the reagents raw rubber and free sulfur become exhausted as the reaction proceeds and the heat of combustion available may be insufficient to raise the mass to the explosion point, so that a sys-

tem, which, according to the simple theory, would appear to be just unstable may be stable, though the temperature rise may exceed 11°C . In the case of the higher temperatures, heat may be absorbed also in decomposing the rubber.

(c) The outer layers of the sheet are in practice not inert, but contribute to the internal production of heat. The heat production therefore varies through the sheet so that the temperature gradient is not uniform as assumed.

It would, of course, be desirable to develop a complete mathematical solution of the problem if that were possible. In order to do that it would be necessary to express in simple algebraical form the relations between temperature, degree of combination of sulfur, and rate of production of heat so that temperature could be calculated as a function of time.

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Effect of Pressure on the Dielectric Constant, Power Factor, and Conductivity of Rubber-Sulfur Compounds

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I. INTRODUCTION

This paper reports the results of a study on the effect of pressure on the dielectric constant, power factor, and conductivity of rubber-sulfur compounds, and is the third paper of a series dealing with the electrical properties of rubber-sulfur compounds.¹ The previous papers dealt with the effect of sulfur content, temperature, and current frequency on these electrical properties. The results reported in the present paper have been corrected for changes in the dimensions of specimens caused by changes in pressure. The required data for making these corrections were obtained from a detailed study of the compressibility of rubber-sulfur compounds which has recently been completed.²

II. METHOD OF DETERMINING ELECTRICAL PROPERTIES

The specimens were made in the form of insulation on wires in order that they might be put in a pressure apparatus consisting of heavy pipes. Each material under test was formed into an insulating cylinder around the wire. The specimen was placed in the pressure apparatus in such a way that the wire core was used as one electrode and the pressure medium as the other. This made a cylindrical capacitor having the material under test as the dielectric. The capacitance, power factor, and conductance of this capacitor were measured when the various pressures were applied.

The dielectric constant, K , of a material is given by the equation:

$$K = AC \quad (1)$$

where C is the capacitance of the capacitor having this material as the dielectric, and A is the shape factor of the capacitor. For certain shapes of the capacitor, A may be readily computed from easily determined dimensions and the dielectric constant obtained from a measurement of the capacitance. However, the specimens used in this investigation were not sufficiently uniform and symmetrical to permit the computation of A . Therefore, an indirect method was used in the determination of A . The dielectric constant of the material was determined by means of flat specimens at atmospheric pressure and 25° C. as described by Curtis, McPherson, and Scott.³ The flat specimen for this purpose usually was made at the same time and from the same batch of material as the cylindrical specimen. The value of A for the cylindrical specimen could then be computed from the capacitance measured in the pressure apparatus at atmospheric pressure and 25° C. and from the value of K obtained from the flat specimen.

The conductivity, γ , of a material is given by the equation:

$$\gamma = BG \quad (2)$$

where G is the conductance of the specimen and B is the shape factor for conductivity. When the electric field is entirely within the dielectric, the shape factor for conductivity is connected with the shape factor for dielectric constant by the equation:

$$B = \frac{10^{21}A}{4\pi v^2} = \frac{A}{11.31} \quad (3)$$

where A is the shape factor for dielectric constant when the capacitance is measured in micromicrofarads, and v is the velocity of light in centimeters per second.⁴

The shape factors were corrected for changes in the dimensions of the specimens due to the compressibility of the materials. The compressibility of the copper or aluminum, of which the core was made, was so small that the effect of the change in the dimensions of the core was negligible. Correction was thus made only for the change in dimensions of the rubber, using the values of compressibility given in a former paper.⁵

III. PREPARATION OF SPECIMENS

Each of the carefully mixed rubber-sulfur compounds was formed in a seamless sheath about a wire. Some of the specimens were vulcanized in steam, while the rest were vulcanized in an inert gas. Those vulcanized in steam were dried before measuring.

1. Materials Investigated

The rubber specimens investigated were vulcanized compounds of rubber and sulfur ranging in composition from 0 to 32 per cent of sulfur. The percentages of sulfur were so chosen that the difference in sulfur content between successive specimens was in no case greater than 6 per cent and in most cases it was 2 per cent or less. Three varieties of rubber were used, up-river fine Para, smoked sheet, and purified rubber. The purified rubber was obtained by the process described by McPherson.⁶

The gutta-percha specimens were cut from a cable which had been obtained from a cable manufacturing company in England. This cable had been stored in water since its manufacture about 18 months before.

2. Compounding of Rubber

The rubber was usually mixed with the sulfur on a roll mill in air. In a few cases the mixing was done in an internal mixer in an atmosphere of carbon dioxide. The rubber and sulfur were weighed separately and the batch was weighed after mixing. The weight of the batch seldom differed from the sum of the weights of the constituents by more than 1 part in 1000. Any greater difference was due to a loss of sulfur during the mixing and the requisite quantity of sulfur was added to correct for this loss.

3. Formation of Specimens

Each specimen was formed by applying the rubber-sulfur compound concentrically about a wire by means of a commercial extrusion machine which had been adapted for this particular work. Since the various rubber-sulfur compounds could

be applied smoothly to the wire in very narrow temperature ranges, it was necessary to control the temperature closely. For this purpose thermometers were placed at strategic points on the machine, and an electric heater was added at the point where the insulated wire emerged, since it was not adequately heated by the original equipment. It was necessary to control the temperature by hand, but this could be readily done after a little experience.

4. Vulcanization of Specimens

Most of the specimens were packed in powdered talc and vulcanized in an atmosphere of steam while the others were vulcanized suspended in an atmosphere of dry hydrogen or CO_2 gas. The method of vulcanizing in steam was replaced by a method of vulcanizing in a dry gas when it was observed that some of the sulfur migrated from the rubber to the talc during vulcanization. Subsequent experiments showed that this migration was particularly significant when small samples of high sulfur content were vulcanized in contact with a considerable quantity of fresh talc.

Those specimens vulcanized in steam were coiled in a pan of powdered talc. This pan and its contents were then placed in a steam vulcanizer which had an automatic control on the steam pressure. The steam in the vulcanizer was maintained at the pressure corresponding to the desired vulcanizing temperature.

Those specimens which were vulcanized in an inert gas were placed in a 2-inch pipe, 6 meters in length, which was mounted vertically and which was provided with a steam jacket welded around it. The specimen was fastened at the top and suspended down the length of the pipe. A weight was fastened to the lower end of the specimen to keep it from touching the sides. The gas pressure around the specimen was kept slightly higher than the steam pressure at the vulcanizing temperature. If the pressure on the specimen was not kept above the pressure of the steam at the vulcanization temperature, the specimen became porous. This porosity was probably due to vaporization of the small amount of moisture present in the compound.

The specimens were vulcanized at 150°C . for 4 to 15 hours. These relatively long times of vulcanization were used to assure the combination of practically all the sulfur.

5. Drying of Specimens

The specimens which were vulcanized in steam were carefully dried before electrical measurements were made on them. Two methods of drying were used. Some of the specimens were placed in a sealed tank in which a vessel of concentrated sulfuric acid had been placed. This tank was kept at the temperature of 25°C . while the air in it was kept stirred by a small fan. The specimens were kept in this tank for 2 or 3 weeks. Other specimens were placed in a vacuum desiccator in which a drying agent had been placed. The desiccator was evacuated and the specimens left in this condition for 1 or $1\frac{1}{2}$ weeks. All the specimens were stored in a dry atmosphere until measurements were made.

IV. APPLICATION OF PRESSURE TO SPECIMENS

The specimens, each of which was about 6 meters in length, were put in the pressure apparatus in such a way that one end was fastened to a special plug through which electrical contact was brought to the outside of the apparatus. An insulating compound was placed over the ends of the specimen to insulate the wire core from the pressure medium. The wire was used as one electrode in the electrical measurements while the pressure medium was used as the other.

1. Apparatus for Applying Pressure to Specimens

A schematic drawing of the apparatus used for applying hydrostatic pressure to the specimens is shown in Fig. 1. It consisted of 3 parallel steel pipes 6 meters long of the grade known commercially as "double extra heavy." These pipes were connected together and to the pump and pressure gauge by means of the proper fittings. The free end of each pipe was about 13 cm. lower than the other end, which allowed the air to be removed from the system at the plug opening at the top of the apparatus.

This apparatus was designed so that either water or mercury could be used as the pressure medium around the specimen. The lowest pipe was provided for use with mercury. It was made the lowest part of the apparatus so that mercury could be

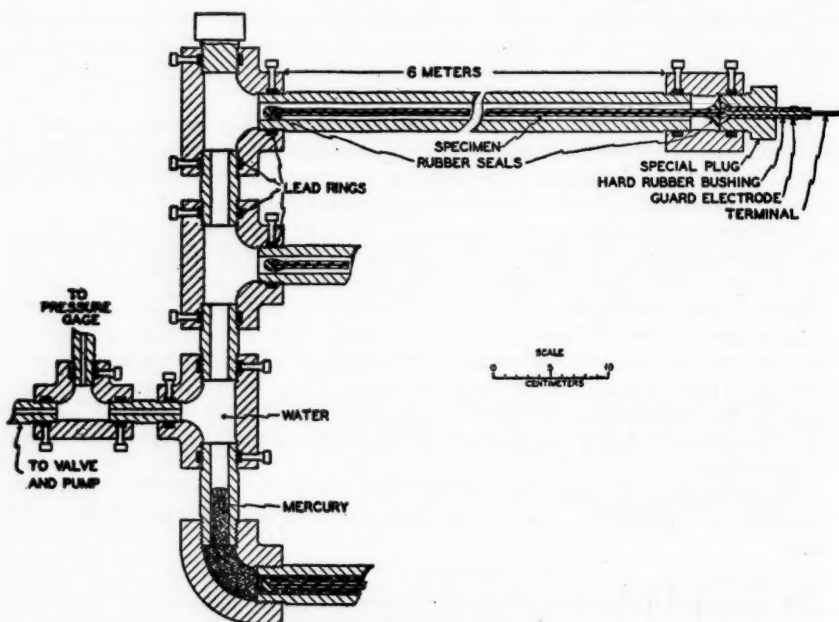


Figure 1—Apparatus for Applying Pressure to Rubber Specimens While Electrical Measurements Are Being Made on Them

placed in it around the specimen, and yet the pressure could be transmitted from the pump to the surface of the mercury by water. The mercury was introduced through the opening in the top of the apparatus by means of a long-stemmed funnel. An electrical-contact system was used to determine when the proper level had been reached.

To facilitate the making of tight joints lead rings were used in the fittings wherever possible. The lead was forced firmly against the threads of the pipe by the set screws. Lead rings, however, could not be used in the part of the apparatus where mercury was used because of the action between mercury and lead. In this case the joints were made tight by heating the parts, applying "universal" wax and screwing them together while still hot. It was found possible to make the joints so tight that when a pressure of 700 bars⁷ was applied to the system and the valve closed, the pressure would not decrease by more than 30 bars in 24 hours.

2. Mounting of Specimens

The specimens were mounted as shown in Fig. 1. The specimen extended down the length of the pipe and was connected at one end to the special plug. This plug, through which electrical contact was made to the core of the specimen, was so designed that the insulated terminal would not creep under the pressure used. A hard-rubber bushing, which was flared at the inner end, was screwed into a hole through the center of the steel plug. The bushing extended about 2.5 cm. beyond the outer end of the steel plug. The insulated terminal consisted of a brass rod which was flared on the inner end. This was screwed into a hole in the hard-rubber bushing. This terminal extended about 2.5 cm. beyond the bushing. A small threaded hole was placed in the flared end of the brass terminal and the wire core of the specimen was screwed into this.

The wire core, which was used as the inner electrode, was effectively insulated from the pressure medium at both ends by covering them with a thermoplastic insulating (DeKhotinsky) cement or a vulcanized-rubber mixture. The thermoplastic cement was used in the earlier measurements. Rubber was used later because it was found to be more reliable and durable.

The thermoplastic cement was applied by preheating the parts and working the softened material into place. When this material was used the coupling as well as the plug was removed from the pipe. The core of the specimen was attached to the inner end of the terminal in the plug. The coupling and plug were then heated to about 150° C. and melted cement was poured over the face of the plug and around the specimen to a depth of about 2 cm. The cement was applied to the loose end of the specimen by heating it and working a ball of warm cement over it.

The rubber compound which was used to insulate the ends of the specimen core from the pressure medium was a soft, easily worked compound designed for rapid vulcanization. When this was used only the special plug was removed from the pipe. The end of this plug was coated with a thermoprene cement known commercially as Vulcalock cement. After the core of the specimen had been attached to the terminal of the plug, the soft unvulcanized rubber compound was worked around the specimen and over the end of the plug, as shown in Fig. 1, with the aid of a little heat. A small ball of the rubber was also worked over the loose end of the specimen. The loose end and the plug were placed in an oven in such a way that only a few centimeters of the specimen were exposed to the heat of the oven. The oven was kept at a temperature of about 125° C. until the compound was vulcanized.

V. ELECTRICAL MEASUREMENTS

The electrical measurements made on the specimens under pressure were the capacitance, power factor, and conductance.

1. Capacitance and Power Factor

The capacitance and power factor were measured at 1000 cycles per second by means of the modified Rosa bridge described by Scott, McPherson, and Curtis.⁴ The capacitance between the wire core and the pressure medium surrounding the specimen was measured by a substitution method. Connections were made to the pipes and to the insulated terminal of the plug. This measurement included the capacitance in the plug, which was found to be of the order of 3 micromicrofarads. This excess capacitance was probably approximately counterbalanced by the decrease in capacitance of the specimen due to the sealing compound covering short lengths of the specimen at each end. About 1 cm. was covered at the loose end, while about 1.5 cm. was covered at the other end. While the exact error in capaci-

tance due to the sealing compounds could not be determined, it was opposite in sign to the error, due to neglecting the capacitance in the plug, and it was assumed that the resulting error was negligible in comparison to the capacitance of the specimen, which was usually about 2000 micromicrofarads.

2. Conductance

The conductance was measured by means of the direct deflection method described by Scott, McPherson, and Curtis.⁹ A potential of 300 volts was used for this measurement. The readings were taken at the end of 1 minute after the potential was applied. Each specimen was short-circuited for 2 minutes before a measurement was made in order to eliminate the effect of the residual charge from previous electrifications. The guard electrode used in this measurement consisted of a piece of tinfoil wrapped tightly around the hard-rubber bushing as shown in Fig. 1. A fine wire was wrapped around the tinfoil to hold it in place and to afford a means of connecting it to the ground.

VI. RESULTS

The results were obtained under several different conditions. However, it was not thought advisable to divide the results into groups according to the different conditions which existed, since the variation between groups was no larger than that between the individual specimens of a single group. The composition of the various specimens and the conditions under which they were measured are given in Table I. The percentages of sulfur are given in the first column and the variety of rubber used is given in the second column. The third column gives the number of specimens of each which were measured. The kind of wire used as the core is given in the fourth column, and the method of vulcanization is given in the fifth column. The sixth column shows whether water or mercury was used as the pressure medium. The seventh column shows which of the specimens had the temperature controlled at 25° C. during measurement, while the last column gives the gauge which was used to measure the pressure.

The specimens were made from three varieties of rubber, as was mentioned previously. No consistent difference between the specimens made from upriver fine Para and smoked sheet could be observed. As pointed out by Scott, McPherson, and Curtis, the electrical properties of specimens made from purified rubber were slightly different from those made from unpurified rubber.¹⁰ However, it was found that the change with pressure was about the same, regardless of whether the rubber was purified or not. Because of this fact and because only four specimens made from purified rubber were measured, the results for these specimens were not grouped separately.

Two kinds of wire were used in preparing the specimens. Tinned copper wire was used in the earlier specimens, but when it was found that the tinning did not prevent action between the copper and the sulfur in the rubber, this was discarded in favor of aluminum wire. Comparison of results, however, failed to disclose any consistent difference between specimens made with the two kinds of wire.

Most of the pressure measurements were made with a pressure gauge of the Bourdon tube type. This instrument was found to have errors as large as 10 per cent, which depended on whether the pressure had just been increased or decreased. The pressures were measured with the more accurate resistance pressure gauge, described in a former paper, when this instrument became available.¹¹ However, measurements were made with this gauge in only four cases. The measurements made with the Bourdon tube gauge were corrected as best they could be but the inaccuracy of the pressure measurements is one of the sources of error in the results.

TABLE I
COMPOSITION OF SPECIMENS AND CONDITIONS OF MEASUREMENT

Combined Sulfur ^a Per Cent	Rubber Used	Number of Speci- mens	Wire Core	Vulcanized in—	Pressure Medium	Tempera- ture Control	Pressure Gauge
0	Fine Para	1	Copper		Mercury	None	Bourdon
2	Fine Para	3	Copper	Steam	Mercury	None	Bourdon
4	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
4.9	Fine Para	2	Copper	Steam	Water	None	Bourdon
5 ^b	Smoked sheet	1	Copper	Steam	Water	None	Bourdon
5.4	Smoked sheet	2	Copper	Steam	Water	None	Bourdon
6	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
6	Purified	1	Aluminum	CO ₂	Mercury	25° C.	Resistance
8	Purified	1	Aluminum	CO ₂	Mercury	25° C.	Resistance
8	Fine Para	1	Aluminum	Hydrogen	Mercury	None	Bourdon
8	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
8.5 ^b	Smoked sheet	1	Copper	Steam	Water	None	Bourdon
10 ^b	Smoked sheet	2	Copper	Steam	Water	None	Bourdon
10	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
10	Fine Para	1	Aluminum	Steam	Mercury	None	Bourdon
10	Purified	1	Aluminum	CO ₂	Mercury	25° C.	Resistance
11.5 ^b	Smoked sheet	1	Copper	Steam	Water	None	Bourdon
12	Purified	1	Aluminum	CO ₂	Mercury	25° C.	Resistance
12	Fine Para	1	Aluminum	Hydrogen	Mercury	None	Bourdon
13 ^b	Smoked sheet	1	Copper	Steam	Water	None	Bourdon
13.5	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
13.5	Fine Para	1	Aluminum	Steam	Mercury	None	Bourdon
14.5 ^b	Smoked sheet	1	Copper	Steam	Water	None	Bourdon
16	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
16 ^b	Smoked sheet	1	Copper	Steam	Water	None	Bourdon
17.5 ^b	Smoked sheet	1	Copper	Steam	Water	None	Bourdon
18	Fine Para	2	Copper	Steam	Mercury	None	Bourdon
18.1	Fine Para	2	Copper	Steam	Water	None	Bourdon
19	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
19	Fine Para	1	Aluminum	Steam	Mercury	None	Bourdon
19 ^b	Smoked sheet	1	Copper	Steam	Water	None	Bourdon
20	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
22	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
24 ^b	Smoked sheet	1	Copper	Steam	Water	None	Bourdon
26	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
32	Fine Para	1	Copper	Steam	Mercury	None	Bourdon
32	Smoked sheet	2	Copper	Steam	Water	None	Bourdon

^a The sulfur content was assumed to be that which was mixed into the compound in all cases, except for 4.9, 5.4, and 18.1 per cent of sulfur. These specimens were analyzed for sulfur when it was discovered that sulfur migrated to the talc during vulcanization in steam. The other specimens vulcanized in steam were not then available for analysis.

^b These specimens were not measured through a pressure cycle until after they had been under pressure for about a month.

Another source of error in the results is the lack of temperature control. Most of the measurements had been made before the importance of temperature control was realized. Only the last four specimens were measured under controlled-temperature conditions. The temperatures of the other specimens varied from 18.5° to 26.5° C., with most of the measurements being made at temperatures between 20° and 22° C.

The two pressure media, water and mercury, were used so that the possible effect

of water absorption might be studied. Measurements with mercury as the pressure medium gave results for the specimen in the dry condition. With water as the pressure medium the effect of progressive water absorption could be studied.

1. Dielectric Constant

The effect of pressure on the dielectric constant is shown in Fig. 2, where the dielectric constants at atmospheric pressure (approximately 1 bar) and 700 bars are plotted as functions of the sulfur content. These curves were obtained from measurements made on the 34 specimens immediately after they had been

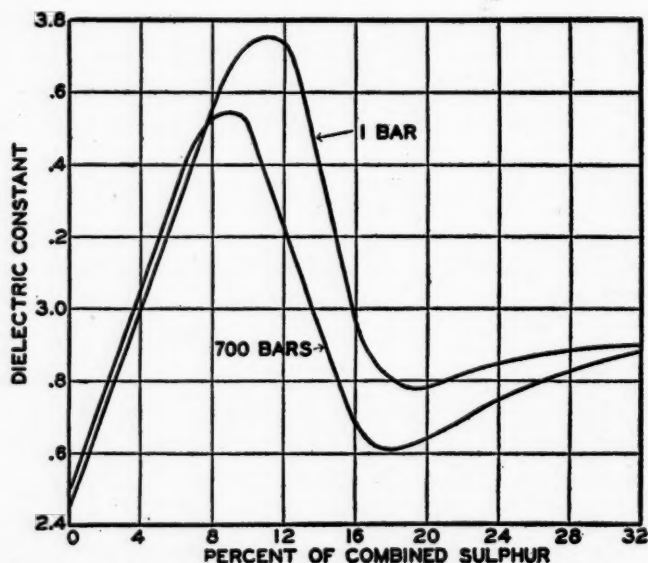


Figure 2—Change of the Dielectric Constant of Rubber-Sulfur Compounds with Sulfur Content, at 1 and at 700 Bars

placed in the apparatus. The curve for 1 bar is the same as that reported in the paper by Curtis, McPherson, and Scott.¹² The irregularity of the measured values at 1 and 700 bars is about the same. At 700 bars two-thirds of the specimens yielded values which agreed with the values given by the curve within 1 per cent. The difference was greater than 2 per cent in only six cases. The maximum difference was 6 per cent which was obtained for the specimen containing 18.1 per cent of sulfur.

Increasing the pressure moved the maximum to lower percentages of sulfur and decreased the height of the maximum. This is the same effect as was obtained by decreasing the temperature as reported by Scott, McPherson, and Curtis.¹³ A change of 700 bars pressure had the same effect as a change in temperature of 12° to 20° C., the average being about 16° C. The dielectric constant for specimens containing up to about 7.5 per cent of sulfur was increased slightly by pressure. For higher percentages of sulfur the dielectric constant was decreased by pressure.

The maximum change with pressure occurred for about 12 per cent of sulfur, while for 32 per cent of sulfur the decrease with pressure was small.

The dielectric constant was, in most cases, a linear function of the pressure between 1 and 700 bars pressure. There were two ranges of sulfur content where it was not a linear function of the pressure, one range being between about 8 and 10 per cent of sulfur and the other being between about 16 and 24 per cent of sulfur. The results for a few representative specimens are shown in Fig. 3, where the dielectric constants are plotted against the pressure. Two of these, 0 and 4 per cent of sulfur, were selected from the sulfur range where the dielectric constant was increased by pressure. The total increase for a pressure change of 700 bars was small, but the increase of the dielectric constant with pressure was uniform. The specimen containing 8 per cent of sulfur came at about the boundary between the

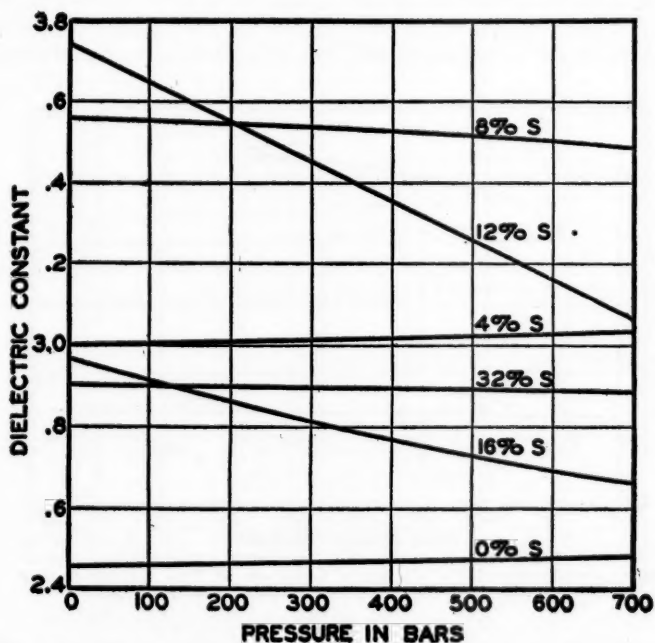


Figure 3—Change of the Dielectric Constant of Various Rubber-Sulfur Compounds with Pressure

sulfur range where the dielectric constant increased with pressure and the sulfur range where the dielectric constant decreased with pressure. This was also in one of the ranges where the dielectric constant was not a linear function of the pressure. The change with pressure was small for this specimen, but was larger at the high pressures than at the low pressures. Three specimens, 12, 16, and 32 per cent of sulfur, were selected from the sulfur range where the dielectric constant decreased with pressure. For 12 and 32 per cent of sulfur, the dielectric constant was a linear function of the pressure, but for 16 per cent of sulfur, the change with pressure became less as the pressure was increased.

The specimens for which water was used as the pressure medium were kept under pressure for a month or more to determine the effect which this would have on the change of the electrical properties with pressure. It was found that for the specimens containing low percentages of sulfur the electrical properties changed with

time, under pressure, but that for specimens containing over 18 or 20 per cent of sulfur there was little change. The results for two representative specimens are shown in Figs. 4 and 5. Figure 4 shows the change of the dielectric constant of specimens containing 4.9 and 32 per cent of sulfur with time under 655 bars pressure. The dielectric constant of the specimen containing 4.9 per cent of sulfur increased rapidly with the time under pressure for the first few days, after which the change with time became much less. This curve is similar to the one published by Curtis and McPherson¹⁴ for a flat specimen at atmospheric pressure, except that a period of days was required for the dielectric constant to approach constant value, while only hours were required in the case of the flat specimen. This difference in time may, in part, be accounted for by the fact that the flat specimen was thinner than the cylindrical specimen and that it was exposed to water on both sides while the cylindrical specimen had only one surface exposed to the water. The difference in composition of the specimens may have been an added factor in this difference in

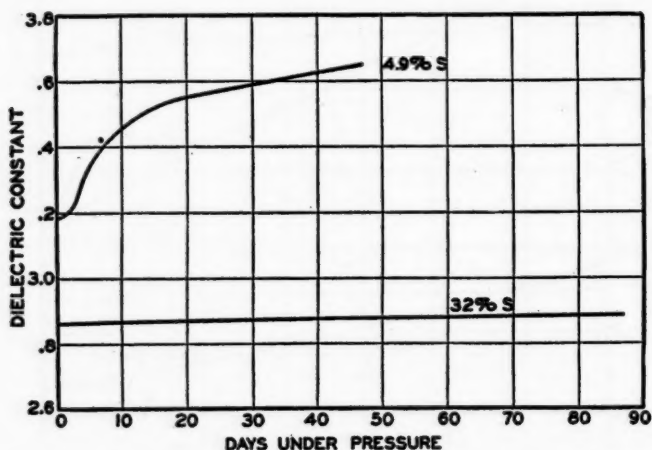


Figure 4—Change of the Dielectric Constant of Two Rubber-Sulfur Compounds with Time under 655 Bars Pressure in Water

time. The curve in Fig. 4 is of the same type as that obtained by Lowry and Kohman¹⁵ for absorption of water under pressure. The change of the dielectric constant with time under pressure, therefore, seems to be a function of the water absorption alone.

The dielectric constant of the specimen containing 32 per cent of sulfur did not change materially with time under pressure. This was to be expected if the dielectric constant is a function of the water absorption, since hard rubber absorbs very little moisture.

Figure 5 shows the manner in which the dielectric constant of the specimen containing 4.9 per cent of sulfur changed with pressure after various lengths of time under pressure in water. The curves are practically parallel, which shows that the effect of pressure is about the same regardless of the time that the specimen has been under pressure. If the only effect of continued pressure under water is the absorption of water by the rubber, then this is equivalent to saying that the effect of pressure is about the same regardless of the amount of water absorbed. The dielectric constant of the specimen containing 32 per cent of sulfur changed so little

with time under pressure that no curves showing the effect of pressure are given other than the one in Fig. 3.

A few specimens were kept under pressure in mercury for about a month. The dielectric constant increased only slightly during this time and this small change was probably not significant.

2. Power Factor

The effect of pressure on the power factor is shown in Fig. 6, where the power factors at 1 and 700 bars are shown as functions of the sulfur content. These curves were drawn as average curves through the plotted points. The irregularity of the power factor values was large compared with the irregularity of the dielectric constant values. Of the 34 specimens which were measured, 10 had values of the power factor which differed from the values on the curve by more than 20 per cent. Of

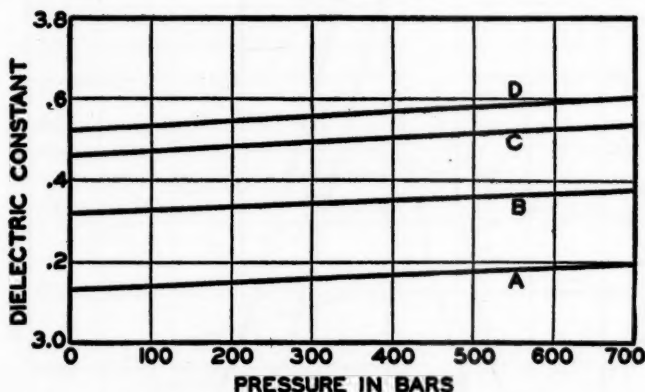


Figure 5—Change of the Dielectric Constant of a Specimen Containing 4.9 Per Cent of Sulfur with Pressure after Different Lengths of Time under 655 Bars Pressure

A, at beginning; B, after 6 days; C, after 18 days; D, after 33 days

these, 5 differed by more than 40 per cent. Two of these latter specimens, 1 of which contained 6 per cent of sulfur and the other 18.1 per cent of sulfur, had power factors which differed from the values on the curve by about 85 per cent. This irregularity was larger than was obtained for the flat specimens at atmospheric pressure.

Increasing the pressure moved the maximum to lower percentages of sulfur. The height of the maximum apparently was not changed by pressure. This was the same type of change that was observed by Scott, McPherson, and Curtis for a change in temperature.¹⁶ The amount of the change brought about by an increase of 700 bars was about the same as was obtained for the temperature changes determined for the dielectric constant.

Although the irregularity of the measured values was large, the character of the change with pressure was consistently that represented by these curves. The power factors of all the specimens containing up to 2 per cent of sulfur were very nearly independent of pressure. The power factors at 700 bars were higher than those at 1 bar for all the specimens containing from 4 to about 12 per cent of sulfur, while

for percentages of sulfur higher than this, the power factors at 700 bars were lower than at 1 bar, with one exception. The values of the power factors of specimens containing 13.5 per cent of sulfur increased with pressure at the low pressures and decreased with pressure at high pressures, so that the values at 700 bars were about the same as those at 1 bar. This does not agree with Fig. 6.

The power factor was a nonlinear function of the pressure in most cases for pressures between 1 and 700 bars. The manner in which the value of the power factor varied with the pressure is shown in Fig. 7, where the power factors for a few representative specimens are plotted against the pressure. The specimen containing no sulfur was selected from the sulfur range where the power factor was unaffected by

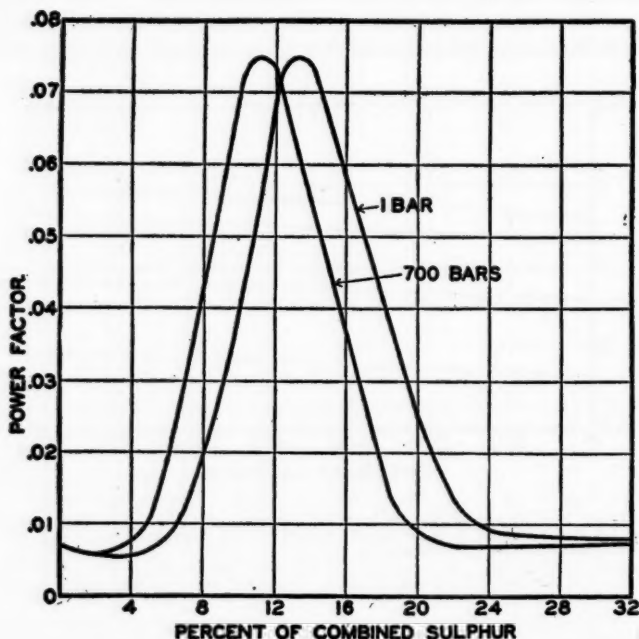


Figure 6—Change of the Power Factors of Rubber-Sulfur Compounds, at 1 and at 700 Bars, with Sulfur Content

pressure. The specimens containing 4 and 8 per cent of sulfur were selected from the range where the power factor increased with pressure. The curves for these are concave upward. The specimen containing 12 per cent of sulfur was in the range where the power factor passed through a maximum with pressure. The curve for this specimen is concave downward and the maximum occurs at about 250 bars. The specimens containing 16 and 32 per cent of sulfur are from the sulfur range where the power factor decreased with pressure. The curve for 16 per cent of sulfur is concave downward, whereas that for 32 per cent of sulfur is concave upward. In only one other case beside those for 0 and 2 per cent of sulfur was there indication that the power factor was a linear function of the pressure. The power factors of 2 of the specimens containing 10 per cent of sulfur were linear functions of the pressure. The power factor of the third, which was made from purified rubber, was not a linear function of the pressure and its curve was concave downward.

The change of the power factor with time under a pressure of 655 bars in water is shown for two specimens in Fig. 8. The power factor of the specimen containing 4.9 per cent of sulfur increased for a few days, and then decreased to a value lower than that at the beginning. This curve is similar to the one published by Curtis and McPherson for a flat specimen.¹⁷ However, the time to reach maximum was quite different in the two cases. It required only about 10 hours to reach maximum for the flat specimen, but required about 9 days for the cylindrical specimen under pressure. As explained in the case of the dielectric constant, the difference in time may be due to the difference in shape and composition. The power factor of the

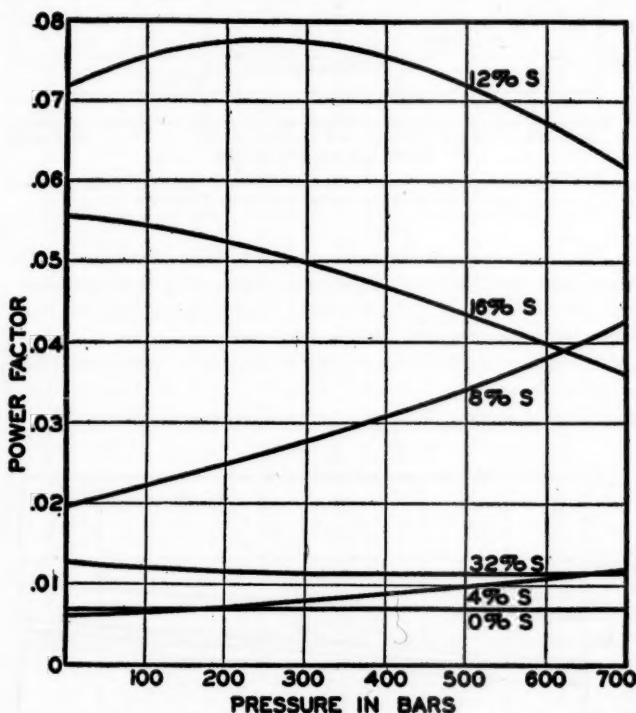


Figure 7—Change of the Power Factors of Various Rubber-Sulfur Specimens with Pressure

specimen containing 32 per cent of sulfur did not change appreciably with time under pressure.

The manner in which the power factor of the specimen containing 4.9 per cent of sulfur changed with pressure after various periods under pressure is shown in Fig. 9. These curves are slightly concave upward, but are approximately equidistant from each other at all pressures. Thus, the only effect of time under pressure was to change the values but not to change the slopes of the curves. The curves for the specimen containing 32 per cent of sulfur were practically unaffected by time under pressure and so no curves are shown for it, except the one in Fig. 7.

3. Conductivity

The effect of pressure on the conductivity is shown in Fig. 10 where the conduc-

tivities at 1 and 700 bars are shown as functions of the sulfur content. These curves show the general average of values, though the irregularity of the measured values was large. About half of the specimens had measured conductivities which differed at 1 or 700 bars from the curve values by more than 40 per cent. Of these, 5 specimens had conductivities which differed from the curve values by more than

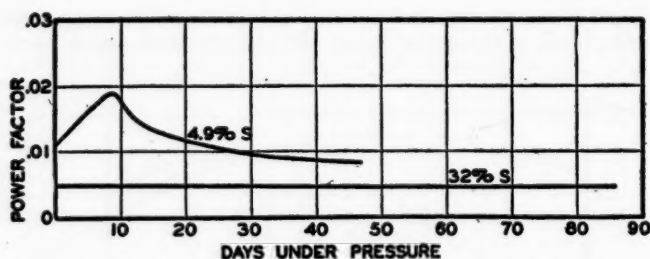


Figure 8—Change of the Power Factors of Two Rubber-Sulfur Specimens with Time under 655 Bars Pressure

60 per cent. In one case the difference was more than 80 per cent. The conductivity of the single specimen containing no sulfur at 1 bar exceeded the value shown on the curve by about 230 per cent. The value shown on the curve is in agreement with the measurements on flat specimens.

The maximum of the conductivity curve was moved to lower percentages of sulfur by increased pressure, as were the maxima for dielectric constant and power factor. This change is in the same direction as was obtained by Scott, McPherson, and

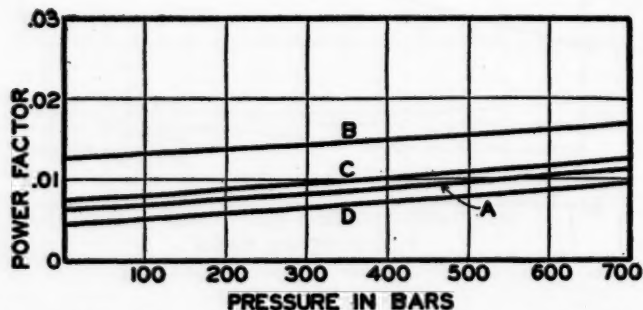


Figure 9—Change of the Power Factor of a Rubber-Sulfur Specimen Containing 4.9 Per Cent of Sulfur with Pressure after Different Lengths of Time under 655 Bars Pressure

A, at beginning; B, after 6 days; C, after 18 days; D, after 33 days

Curtis, for a decrease in temperature.¹⁸ The change with pressure at low percentages of sulfur has no counterpart in the change with temperature as observed by them, since the conductivities of the specimens made from purified rubber, which they used, were about as low in the low-sulfur range as in the high-sulfur range.

Though the irregularity in results was large, the sign of the change with pressure was nearly always that indicated by the curves. The conductivity at 700 bars was lower than at 1 bar for all specimens containing up to 10 per cent of sulfur and above 19 per cent of sulfur. For 12 per cent of sulfur, the conductivity did not

change with pressure. For specimens containing 13.5 to about 19 per cent of sulfur, the conductivity at 700 bars was higher than at 1 bar, except for the specimen containing 18.1 per cent of sulfur.

The general manner in which the conductivity changed with pressure between 1 and 700 bars is shown in Fig. 11, where the conductivities of a number of representative specimens are plotted against the pressure. The specimen containing 4 per cent of sulfur was selected from the low-sulfur range, where the conductivity decreased with pressure. The curve for this specimen is concave upward, as are the curves for all the specimens except one in this range. The curve for one of the specimens containing 2 per cent of sulfur was apparently a straight line. The specimen containing 12 per cent of sulfur came between the two ranges, in one of which the

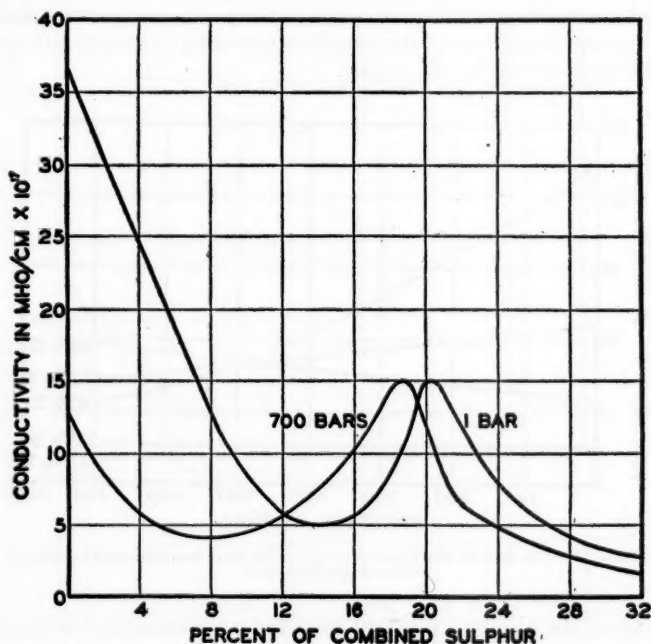


Figure 10—Change of Conductivities of Rubber-Sulfur Compounds at 1 and at 700 Bars with Sulfur Content

conductivity decreased with pressure and in the other increased with pressure. The conductivity of this specimen was independent of pressure. The specimen containing 16 per cent of sulfur was selected from the sulfur range where the conductivity increased with pressure, and the specimens containing 22 and 32 per cent of sulfur were selected from the high-sulfur range where the conductivity decreased with pressure. Except in the first range, the conductivity was generally a linear function of the pressure. The few exceptions are probably not significant since duplicate specimens would have conductivities, one of which was a linear and the other a non-linear function of the pressure.

4. Dielectric Constant, Power Factor, and Conductivity of Gutta-Percha

Two specimens of the gutta-percha used in cable manufacture were measured

under pressure in water. The results are shown in Fig. 12 for comparison with the results on the rubber-sulfur compounds. The dimensions were not corrected for compression of the gutta-percha since it was not known. It probably would not decrease the dielectric constant at 700 bars by more than 2 per cent. The correction for conductivity would be less than the experimental error. It is seen that the dielectric constant is not greatly affected by pressure. The power factor increased with pressure while the conductivity decreased with pressure.

VII. DISCUSSION OF RESULTS

This investigation has been in progress over a number of years and during that time several improvements in technique and methods of measurement were made, as described above. It was not practical to make a complete set of measurements under the improved conditions. It is therefore necessary to keep in mind the variation in conditions in studying the results.

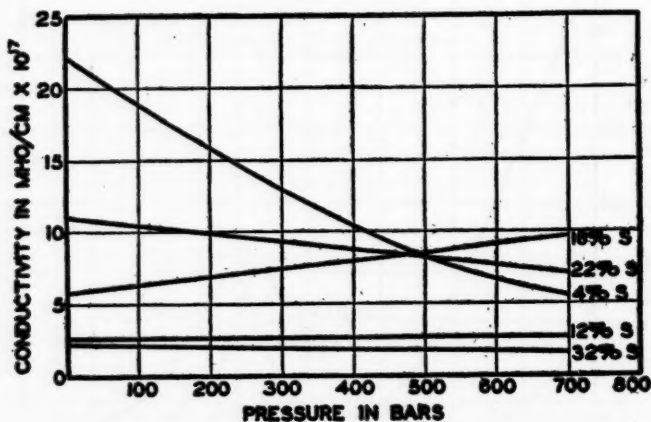


Figure 11—Change of the Conductivity of Various Rubber-Sulfur Specimens with Pressure

The values of the dielectric constant were the most consistent of the electrical properties measured. As mentioned above, the measurements under pressure were made at room temperature for the most part. A study of the change of the dielectric constant with temperature led to the conclusion that the irregularities of the temperature could not explain the irregularities in the dielectric constant.

The irregularity in the power factor determinations was very large compared with that of the dielectric constant and was much larger than was obtained by Scott, McPherson, and Curtis in their work with the flat specimens at atmospheric pressure.¹⁹ A consideration of the temperatures at which the measurements were made led to the conclusion that only a part of the irregularity in power-factor determinations could be accounted for by the diversity of temperatures.

It is possible that a part of the irregularity observed in the values of the electrical properties is due to an inaccurate assignment of composition. The amount of sulfur in the specimen was assumed to be that which was put into the mixture. Late in the investigation it was found that in some cases significant amounts of sulfur migrated from the rubber compound into the talc during vulcanization in steam. Thus, the composition of the cylindrical specimen was not the same as that of the

flat specimen made from the same batch of mixture. Most of the specimens had deteriorated so badly that they had been discarded before it was realized that an analysis should have been made. The six specimens that were vulcanized suspended in an inert gas suffered no significant loss of sulfur during vulcanization. The assigned sulfur contents of the others may be in error by varying amounts. Even this, however, would not explain all the irregularity in the results of the power factor determinations. In two cases, supposedly identical specimens having about the same value of the power factor at 1 bar had quite different values at 700 bars.

The irregularity in the results of the conductivity determinations was no greater than might be expected from such measurements. It is significant, however, that

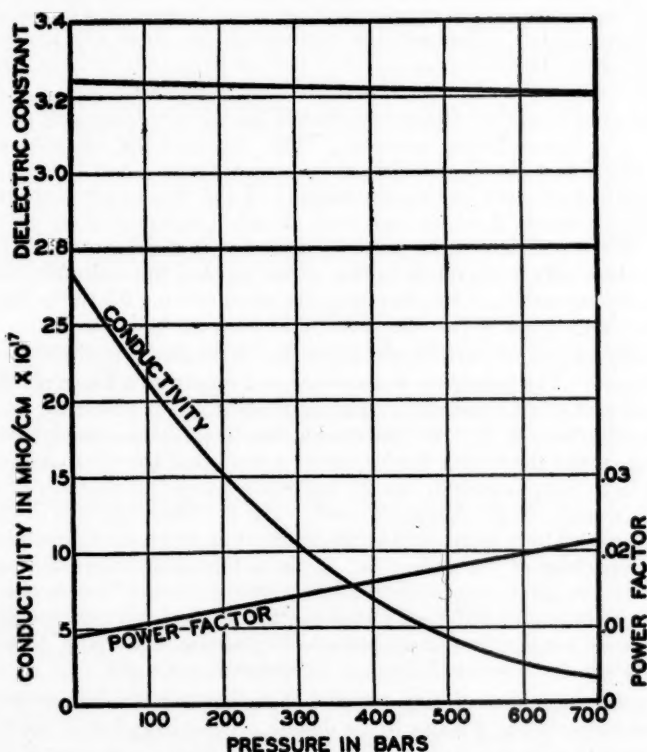


Figure 12—Change of the Dielectric Constant, Power Factor, and Conductivity of Gutta-Percha with Pressure

the value of the conductivity decreased with pressure in rather definite sulfur ranges and increased with pressure in other ranges.

Only a negligible part of the power factor can be accounted for by the 1-minute conductivity. Assuming the specimen having the highest conductivity to be a perfect capacitor in parallel with a conductance equal to the 1-minute conductivity of the specimen, the computed power factor due to this conductance would be about 1×10^{-6} . This is about $1/1000$ of the lowest power factor which was measured.

The outstanding feature of these results is that the effect of pressure is not the same for all ranges of sulfur content. Each of the three electrical properties mea-

sured increased with pressure in certain sulfur ranges and decreased with pressure in other ranges. The changes were such that the maximum for each property was moved to lower percentages of sulfur with increased pressure. It is quite evident from this that some phenomenon other than a change in density is occurring.

These results can be qualitatively explained by the dipole or an equivalent theory as first suggested by Kitchin to explain the changes with temperature.²⁰ Under the dipole theory, the curves for dielectric constant in Fig. 2 are explained as follows: The rubber molecule is nonpolar. The addition of sulfur to the rubber molecules produces dipoles which presumably reside in the carbon-sulfur linkages and which thus increase the dielectric constant by amounts which are proportional to the combined sulfur. This explains the linear relationship between the dielectric constant and percentage of sulfur between 0 and about 9 per cent of combined sulfur at the pressure of 1 bar. However, the hardness of the rubber also increases with the sulfur content. This increases the restrictive forces on the dipoles and at certain percentages of sulfur these forces seriously interfere with the motions of the dipoles so that they cannot readily follow the electric field at the frequency used in the measurement of the dielectric constant. Thus, the dielectric constant is not as large as it would be if the dipoles were able to move freely. As still more sulfur is added the rubber becomes harder, the motions of the dipoles are more restricted and the dielectric constant is thus decreased, though the number of dipoles has been increased. When sufficient sulfur has been added so that the restrictive forces on the dipoles allow only a negligible motion of the dipoles, the dielectric constant is due only to the separation of the charges in the atom and the relatively flat portion of the curve above about 19 per cent of sulfur at 1 bar is obtained.

Scott, McPherson, and Curtis have shown that this curve is modified by changes in temperature.²¹ The maximum is decreased and moved to a lower percentage of sulfur by a decrease in temperature. The same effect was produced by an increase of pressure, as shown in Fig. 2. Decreasing the temperature and increasing the pressure both make the rubber harder, which means that the restrictive forces on the dipoles have been increased. In the low-sulfur range the restrictive forces are still negligibly small for the frequency used. The dielectric constant in this range is slightly increased by a decrease of temperature or an increase of pressure because of the closer packing of the molecules. In the sulfur range where the restrictive forces are large enough to appreciably interfere with motions of the dipoles, that is, above about 8 per cent of sulfur, an increase of the restrictive forces, brought about by a decrease in temperature or an increase in pressure, materially decreases the motion of the dipoles, thereby decreasing the dielectric constant.

On the basis of the dipole theory, the part of the power factor represented by the peaks in the curves in Fig. 6 is due to the dipoles. The energy loss in the dielectric, which is due to the dipoles, is proportional to the product of the amount of motion of the dipole and the resistance to motion which it encounters. Thus, at low percentages of sulfur, the dipole contributes a negligible amount to the power factor since the restrictive forces on the dipole are negligible and the dipole rotates freely with the electric field. The low power factor which is obtained is due to other causes. At high percentages of sulfur the dipole contributes a negligible amount to the power factor since the restrictive forces are so great that only negligible motion of the dipole is possible. Here, again, the low power factor which is obtained is due to other causes. In the intermediate-sulfur range where motion of the dipole and an appreciable resistance to its motion are both present, the power loss due to the dipole is added to the loss due to other causes and a peak is obtained in the power-factor curve.

The peak of the power-factor curve is modified by temperature in a manner similar to pressure. Scott, McPherson, and Curtis have shown that the maximum is moved to a lower percentage of sulfur by a decrease in temperature. It will be seen, from Fig. 6, that an increase in pressure gives the same effect. On the low-sulfur side of the peak, where the restrictive forces are so small that the dipoles are still able to approximately follow the electric field, an increase in the restrictive forces increases the power factor. On the other side of the peak, where the restrictive forces are so large that the dipoles can only partially follow the electric field, an increase in the restrictive forces materially decreases the motions of the dipoles, thereby decreasing the power factor.

The similarity of the behavior of the maximum for the conductivity to that of the power factor suggests the idea that the part of the conductivity represented by the maximum might be due to dipole motion. This would mean that for certain values of the restrictive forces the dipoles rotate so slowly under the force of the applied field that they are still yielding at the end of 1 minute. The change of the restrictive forces on the dipoles by temperature or pressure changes would move the maximum in a manner similar to that shown in Fig. 10. The high values of the conductivity at the low percentages of sulfur are probably due to impurities which can be eliminated by purification of the rubber, since the curve for the conductivity of specimens made from purified rubber and sulfur given by Scott, McPherson, and Curtis does not rise appreciably at the low-sulfur end.

References

- ¹ *Bur. Standards Sci. Paper*, **22**, 398 (1927) S560; *Bur. Standards J. Res.*, **11**, 173 (1933).
- ² *Ibid.*, **14**, 99 (1935).
- ³ *Bur. Standards Sci. Paper*, **22**, 398 (1927).
- ⁴ Since the ratio of the shape factors is the same regardless of the shape of the specimen, this ratio may be derived for the simplest case, i. e., a parallel plate capacitor. For this, neglecting edge effects, $K = C \times \frac{4\pi v^2 d}{10^{21} S} = AC$ and $\gamma = G \times \frac{d}{S} = BG$, where K is the dielectric constant, C is the capacitance in micromicrofarads, d is the thickness, S is the area of the electrode, v is the velocity of light, γ is the conductivity, and G is the conductance. Thus, $\frac{A}{B} = \frac{4\pi v^2}{10^{21}} = \frac{4\pi \times 9 \times 10^{20}}{10^{21}} = 11.31$.
- ⁵ *J. Res. Natl. Bur. Standards*, **14**, 99 (1935).
- ⁶ *Bur. Standards J. Res.*, **8**, 751 (1932).
- ⁷ A bar is defined as 10^6 dynes per square centimeter and is equal to 0.987 normal atmosphere.
- ⁸ *Bur. Standards J. Res.*, **11**, 173 (1933).
- ⁹ See footnote 8.
- ¹⁰ *Bur. Standards J. Res.*, **11**, 173 (1933).
- ¹¹ *J. Research Natl. Bur. Standards*, **14**, 99 (1935).
- ¹² *Bur. Standards Sci. Paper*, **22**, 398 (1927).
- ¹³ *Bur. Standards J. Research*, **11**, 173 (1933).
- ¹⁴ *Tech. Paper Bur. Standards*, **19**, 718 (1925).
- ¹⁵ *J. Phys. Chem.*, **31**, 23 (1927).
- ¹⁶ *Bur. Standards J. Research*, **11**, 173 (1933).
- ¹⁷ *Tech. Paper Bur. Standards*, **19**, 718 (1925).
- ¹⁸ *Bur. Standards J. Res.*, **11**, 173 (1933).
- ¹⁹ *Bur. Standards Sci. Paper*, **22**, 398 (1927).
- ²⁰ *J. Am. Inst. Elec. Eng.*, **48**, 281 (1929).
- ²¹ *Bur. Standards J. Res.*, **11**, 173 (1933).

Semi-Ebonite

Part 2

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In Part 1 (RUBBER CHEM. AND TECH., 8, 554 (1935)) frequent reference was made to the volatile products emitted during the aging of semi-ebonite under different conditions. In this section an experiment is described wherein the various products were detected and some attempt made to estimate the relative amounts of each. The experiment in its original form presented considerable difficulty, and many disappointments were experienced before a modified apparatus was finally adopted.

Experimental Method.—Eight test-pieces, one from each of the accelerated cures (see Part 1), were cut to a convenient size, six inches by one inch. The test-pieces were carefully weighed and their thickness determined as the average of several readings on the micrometer. The strips were suspended from a bent glass rod projecting from a cork-bearing inlet and outlet tubes (see Fig. 5). The cork was then inserted in a clean conical flask and the latter sealed with wax until it withstood a considerable vacuum. The flask was placed in a Geer oven automatically maintained at 70° C. The outlet tube was attached to an absorption train and the inlet tube to a purifying train.

The Absorption Agents.—The choice of these was governed by three factors: firstly, the power to absorb separately from the rest one of the four gases to be detected, hydrogen sulfide, sulfur dioxide, carbon dioxide and moisture; secondly, the ability to form an additive compound with the gas to make possible a simple estimation of the very small quantities likely to be evolved; and, thirdly, the independence of the agents before and after it. Many agents were considered and carefully tested; the individual detection of sulfur dioxide and carbon dioxide proved most difficult, good solvents for the one being almost as effective in absorbing the other.

The absorption train comprised (a) a large U-tube containing fine granular calcium chloride to remove moisture; (b) a large U-tube containing sifted pumice stone saturated with a concentrated solution of copper sulfate and evaporated to dryness at 160° C. to remove hydrogen sulfide; and (c) three potash bulbs containing acidulated silver sulfate solution (1/25 E) to remove sulfur dioxide, and two tubes containing calcium chloride; and then (d) three potash bulbs containing 60 per cent caustic potash solution to remove carbon dioxide. The train was completed with a tube containing calcium chloride.

As the sulfur dioxide and hydrogen sulfide evolved during the aging amounted approximately to one volume in ten thousand volumes of *dry* air it was assumed that separate existence of these gases was possible, as was subsequently proved.

The purifying train, similar in all respects to the absorption train, was connected to the inlet tube of the flask containing the rubber specimens to make sure that none of the gases to be estimated entered the absorption agents via the oxidizing medium, the air.

An automatic valve control (see Fig. 5) was included to preserve an even flow of air through the apparatus despite inevitable changes in the water pressure. This control was connected through a filter flask to the water pump.

Procedure.—The apparatus was first proved free from leakage under a consider-

able vacuum and then air was drawn through to remove all traces of the gases to be detected. Each absorption unit was sealed and removed, dried and weighed and reassembled in the apparatus. The semi-ebonite was allowed to age for 20 days, air being drawn through periodically. After each flow the absorption units were removed and weighed as before. Small yet definite changes in weight were observed but the size of the apparatus rendered a quantitative estimation unreliable.

The thickness of each specimen was determined before and after the experiment (Table XXII).

The density of each specimen was determined before and after the experiment (Table XXII) by the method depending upon the principle of Archimedes.

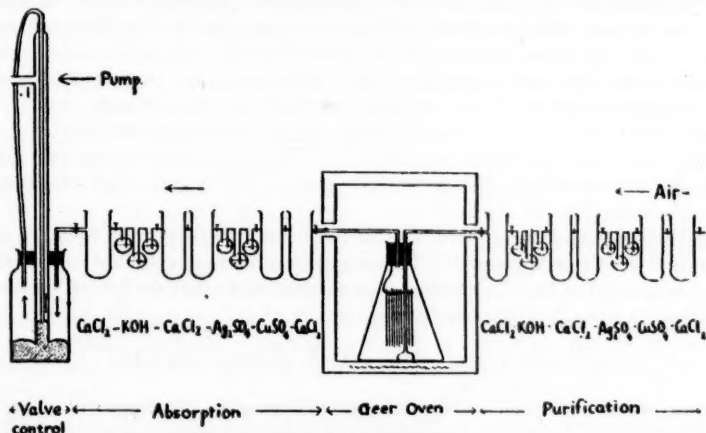


Figure 5—Apparatus to Determine the Volatile Products Evolved during Oven-Aging of Semi-Ebonite

Experimental Results and Calculations.—The average increase in weight of the specimens after 458 hours' aging in the flask was a trifle lower than that recorded for the corresponding period of oven-aging, described in Part 1, where the samples were not enclosed. As the humidity of the air in this case was kept at zero, this may explain the difference observed. The comparative results are shown in Table XXII and reveal that the aging was not materially affected by the limitations of the ap-

TABLE XXII
PHYSICAL CHANGES OBSERVED AFTER 458 HOURS IN THE GEER OVEN

Parts per 100 of Rubber Sulfur	Nonox	Increase in Weight in G. per Sq. M. Specimen		Initial	Density Final	Increase	Thickness M. M. S.	
		Enclosed Specimen	Not Enclosed				Initial	Final
25	0	1.76	2.02	1.079	1.086	0.65	2.47	2.48
25	1	1.91	2.19	1.076	1.084	0.74	2.36	2.37
22.5	0	2.70	2.74	1.065	1.073	0.75	2.45	2.46
22.5	1	3.11	2.79	1.066	1.074	0.75	2.56	2.56
20.0	0	3.37	3.31	1.048	1.056	0.80	2.54	2.55
20.0	1	3.24	3.92	1.050	1.080	0.92	2.40	2.41
17.5	0	3.51	4.07	1.042	1.051	0.87	2.42	2.44
17.5	1	3.78	4.55	1.044	1.053	0.87	2.38	2.40
Initial weight of specimens					79.3782 g.			
Final weight of specimens					79.5798 g.			
Increase in weight					0.2016 g.			

paratus employed. Similar observations concerning the effect of Vulcafor resin, Nonox, and the sulfur content upon the increase in weight with aging described in Part 1 applied equally here.

The air was dried before actual entry into the flask containing the specimens. The increase in weight of the specimens, therefore, could not be ascribed to changes in the humidity.

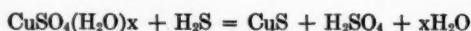
The increases in weight of the absorption units and the changes in appearance observed in the absorption agents described below proved conclusively that water, sulfur dioxide, carbon dioxide, and hydrogen sulfide were evolved during oven-aging.

The originally fresh dry calcium chloride in the first tube showed obvious signs of the presence of water and the increase in weight was relatively large. A small deposit and a corresponding increase in weight was apparent in the silver sulfate solution due to the formation of an additive compound with the sulfur dioxide that entered it. A small increase in weight of the bulbs containing caustic potash showed that a quantity of carbon dioxide was evolved from the semi-ebonite.

In each case the increase in weight diminished as the aging proceeded.

Peachey and Leon (*J. Soc. Chem. Ind.*, 37, 53T (1918)) showed that raw and vulcanized rubber and balata exposed to oxygen at 85° C. evolved appreciable quantities of carbon dioxide.

In the tube containing copper sulfate a slight loss in weight was recorded, though the brown stain characteristic of a fine deposition of copper sulfide extended some four inches along the tube. The loss was attributed to further loss of moisture by the hydrate as a result of the reaction:



A slow current of hydrogen sulfide was passed through a duplicate tube containing an equal portion of the original pumice stone saturated with copper sulfate until an equivalent deposition of copper sulfide had occurred. From observations upon the rate of flow the amount of hydrogen sulfide collected in the first tube was calculated and the change in weight of the next absorption unit, silver sulfate solution, corrected for the moisture carried forward.

A summary of these results is shown in Table XXIII.

TABLE XXIII

Volatile Product	Mass Evolved in G.		Elements	Contribution by the	G. per
	Actual	Per Square Meter		Semi-Ebonite Actual Mass	Sq. M.
Water	0.7980	11.571	Hydrogen	0.0887	1.286
Sulfur dioxide	0.0190	0.276	Sulfur	0.0095	0.138
Carbon dioxide	0.0222	0.322	Carbon	0.0061	0.088
Hydrogen sulfide (calculated)	0.0106	0.154	Hydrogen } Sulfur }	0.0106	0.154
Totals	0.8498	12.323		0.1149	1.666

The semi-ebonite showed a net increase of 0.2016 gram in spite of the loss of 0.1149 gram calculated above. Assuming that these two figures covered the whole oxidation process as far as the changes in weight were concerned, the total weight of non-volatile products formed during 458 hours in the oven was 0.3165 gram, equivalent to an increase of 4.589 grams per square meter of surface exposed.

From Fig. 1, Part 1 (*loc. cit.*), it was observed that the increase in weight with oven-aging was fairly rapid for the first 1250 hours and proceeded at approximately

one-fifth of the rate during the subsequent 4750 hours. On this basis the increase in weight due to the formation of non-volatile oxidation products in the first 6000 hours' oven-aging amounted to 22.05 grams per square meter and the loss due to the evolution of volatile products to 11.38 grams per square meter of surface of semi-ebonite. The formation of non-volatile and volatile products diminished as the aging proceeded.

Fry and Porritt (*India-Rubber J.*, **73**, 307 (1929)) found that hydrogen sulfide is evolved during the exposure of ebonite to diffused light at ordinary temperatures. The evolution was increased by rise in temperature and the action of sunlight. They ascribed the evolution of this gas to the decomposition of the rubber-sulfur compound. They noticed the characteristic odor of hydrogen sulfide when specimens of ebonite were rasped. The writer noticed the same odor when samples of semi-ebonite were flexed rapidly over pulleys for long periods. An odor of volatile compounds other than that associated with hydrogen sulfide was referred to by the above writers. It was probable that they detected the sharp odor of sulfur dioxide, for they found the presence of acidic substances, probably sulfuric and sulfurous acids, in the surface oxidized film. This was further supported by the work of Yamazaki (*J. Soc. Rubber Ind., Japan*, **5**, 79 (1932)), who found that, during the aging of vulcanized rubber, some sulfur was converted into sulfuric acid. Cummings (*J. Research Bur. Standards, U. S. A.*, **9**, 163-74 (1932)), showed that the evolution of hydrogen sulfide increased with temperature (*cf.* Fry and Porritt) and that it was proportional to the sulfur content. This may be compared with the observation in Part 1, that samples containing higher proportions of sulfur showed a lesser net increase in weight. Further, with higher ratios of sulfur to rubber the emission reached a maximum. He found that moisture was evolved during the aging of vulcanized rubber.

The Effect of Oven-Aging upon the Density of Semi-Ebonite.—The specimens in the sealed flask showed no appreciable change in thickness after 458 hours' accelerated aging (see Table XXII); a slight increase was recorded where such a change did occur. Thus there was a slight increase in volume or none at all. During this period the density (Table XXII) increased from an average value of 1.059 to an average value of 1.067, an increase of 0.79 per cent, while the weight of the specimens increased from 79.3782 to 79.5798 grams, an increase of 0.25 per cent. The density thus showed an increase three times as great as the increase in weight during the same time, a discrepancy not explained by a corresponding decrease in volume. The only other explanation that appeared at all reasonable was that, disintegration occurring, porosity of the surface of the rubber increased as a result of the aging. In the method employed for determining the density of semi-ebonite, an increase in porosity of the surface would have resulted in a lesser volume of water being displaced and the proportionately higher value for the density being obtained. This increase in porosity due to surface disintegration was, in effect, a decrease in volume that a micrometer could not be expected to show. This porosity of the surface was not visible to the eye in the case of accelerated aging, but was referred to with natural exposed aging in Part 1.

The Mechanical Testing of Semi-Ebonite.—The mechanical testing of semi-ebonite presented considerable difficulty. Semi-ebonite has been compared with leather-like rubber products and the hope tacitly expressed that the former might prove an efficient substitute for leather. The two most important qualifications for such a product must be resistance to wear and flexibility.

The Abrasion Test.—In this test a small disc of the material was placed upon a loaded axis and allowed to revolve freely against a moving abrasive surface. The semi-ebonites softened considerably on heating, and friction with the abrasive sur-

face very soon softened the edge to such an extent that the disc began to collapse. With a material to be subjected to heavy and continuous abrasive action, this spreading effect would be a serious disadvantage. The normal use of footwear involves only intermittent abrasion and slight spreading would not prove a serious drawback. The plastic flow is sufficient to enable the semi-ebonite to assume the shape of the foot and to be nailed to the shoe.

Wearing Tests.—A number of soles for shoes only one-tenth of an inch thick were cut from the accelerated products containing $22\frac{1}{2}$ and 25 parts of sulfur per 100 of rubber and worn by people engaged in work involving heavy wear. These included

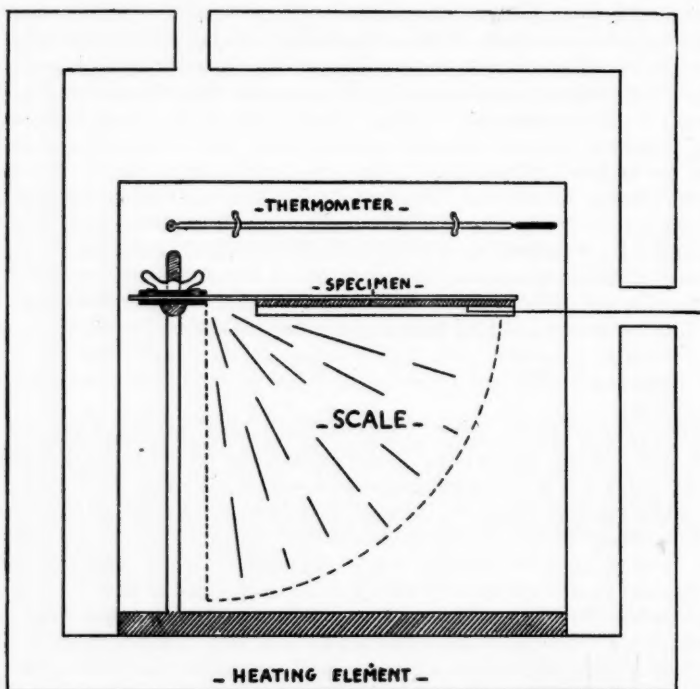


Figure 6—Apparatus Used in the Bending Test

a waitress, an upholsterer, and the manager of a busy shop. In each case resistances to wear greater than the resistance afforded by leather, and comparable with that of heavily compounded rubber substitutes, were reported over a period of five months. Two faults were observed with the soles, early cracking where the greatest bending occurred and a tendency to slip on a wet surface. A patterned surface or the inclusion of a little filling material would overcome the tendency to slip. Cracking was not observed with samples used as heels nor did they leave black marks upon the floor.

The Bending Test.—It was considered that a simple apparatus for comparing the pliabilities of rubber products should be employed. The following apparatus (Fig. 6) was designed and constructed. From a wooden base, 8 by 3.5 inches, a rigid steel bar, 8 inches long, projected vertically. Over this, through a hole in the short edge

was slipped a brass plate, 3 by 1 inches, and the plate was soldered into position. The rear end of the plate rested in a slot cut in the backboard of the apparatus. A similar plate was held firmly against the lower plate by means of a fly-nut and a wedge inserted in the slot at the rear. A quadrant of a circle of 6 inches radius was described upon the backboard, lines at right angles to and parallel with the brass plates forming the limits. The quadrant was marked in degrees or suitable multiples of degrees. A thermometer was clamped near the upper edge and the apparatus placed in an oven thermostatically controlled.

Procedure.—The test-pieces used were 8 inches long and 1 inch wide. (It is important that they be of standard size and weight.) The specimens were clamped firmly between the plates so that some fixed length (*e. g.*, 5 inches) projected over the quadrant. Until ready the strip was supported by a flap which could be readily dropped. In order that all strips might be tested at a standard temperature these were placed in the oven 30 minutes prior to testing. Each strip was placed in posi-

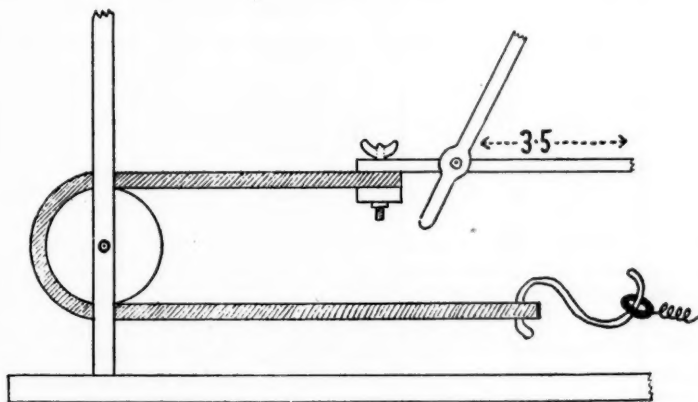


Figure 7—The Flexing Machine

tion, the oven closed, and the temperature readjusted to the standard. The flap was then released and the time taken for the free end of the strip to fall through 10° .

The results obtained with the specimens under examination are shown in Table XXIV.

TABLE XXIV

Parts of Sulfur per 100 of Rubber	25		22.5		20		17.5	
	Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.
Without Nonox	5	46	5	24	1	5	0	34
With Nonox	3	2	1	15	0	7	0	0

A decrease in pliability with increase in sulfur content and an increase in the presence of Nonox were observed experimentally and confirmed by superficial examination.

The advantage of this apparatus lay in the simplicity with which the pliability of rubber products could be indexed. The pliability of vulcanized rubber is sufficiently affected by changes in temperature to make it possible to select the

standard temperatures so that appreciable readings may be obtained with such tough materials as semi-ebonite, and very pliable materials such as overcured soft rubber.

A Tear Test.—Such a test was considered and various forms were studied, but further investigation is necessary.

The Flexing Test.—It was decided after careful consideration that some sort of flexing test would provide the most reliable indication of the leather-like qualities

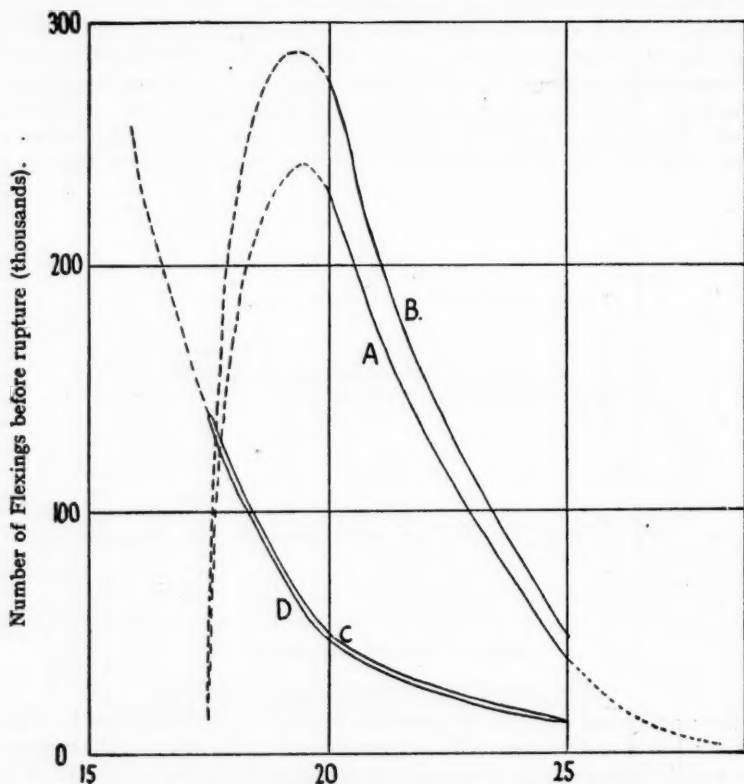


Figure 8—Effect of Sulfur Upon the Flexings before Rupture

Parts of sulfur per 100 of rubber—

- A. Unaccelerated product, not containing Nonox
- B. Unaccelerated product, containing Nonox
- C. Accelerated product, not containing Nonox
- D. Accelerated product, containing Nonox

of the semi-ebonites and their resistance to deterioration on aging. A flexing machine, illustrated in Fig. 7, was improvised from an electrical shaker. The test-pieces described in Part 1 were prepared to fit this machine.

The test-pieces were clamped firmly at the unpierced end between the lower edge of the cradle of the shaker and a flat iron bar supported against it by two wing nuts. Each strip was then passed over and under one of a parallel series of six cycle hubs, acting as pulleys, and one end of a metal hook passed through the hole punched in the strip. The other end of the hook was connected to a spiral spring, 12 inches in length and connected at its far end to a rigid bar running across the width of the

machine. The cradle was then driven rapidly backwards and forwards by means of a suitably geared motor, flexing the rubber strips round the pulleys 200 to 300 times per minute. The flexing was continued until the strips snapped and the total number of flexings calculated. Each test-piece was flexed through 180 degrees for about 5 inches of its length under a tension amounting to approximately 7 lbs. per square inch. Leather used as footwear is flexed through an angle of 10 to 25 degrees under approximately the same load. A great number of test-pieces were treated in this way and flexing values ranging between almost zero and 250,000 were obtained.

The Flexing Strength of the Semi-Ebonites.—In Table XXV and Fig. 8 are summarized the results of tests upon the products under investigation. For purposes of easy comparison the tensile strengths of similar specimens, obtained by means of the Scott machine (see later), are added to Table XXV.

TABLE XXV

Parts per 100 Rubber		Flexings before Rupture		Tensile Strength (Lbs. per Sq. Inch)	
Sulfur	Nonox	Unaccelerated Cure	Accelerated Cure	Unaccelerated Cure	Accelerated Cure
25	0	37,728	13,808	510	1264
25	1	47,926	13,707	455	1220
22.5	0	112,680	15,724	480	1145
22.5	1	129,481	14,084	470	1100
20	0	230,274	48,097	205	516
20	1	275,909	48,289	200	486
17.5	0	12,742	140,643	160	405
17.5	1	11,631	138,696	235	384

It was readily apparent that the number of flexings before rupture increased with decrease in the proportion of sulfur present and with decrease in the toughness of the product. The unaccelerated product containing 17.5 parts of sulfur per 100 of rubber provided a striking exception, clearly supporting the evidence of a visual examination that this is not a true semi-ebonite, but over-vulcanized soft rubber.

A maximum number of flexings before rupture occurred at the lower limit of the semi-ebonites, a small decrease in the proportion of sulfur beyond this limit causing the rapid fall suggested by the dotted lines in Fig. 8. The curves in Fig. 8 suggest that, for unaccelerated cures, between 17.5 and 20 parts per 100 is the lowest pro-

TABLE XXVI

Unaccelerated Product	Parts of Sulfur per 100 of Rubber Accelerated Product	Flexings before Rupture, in Thousands
.....	25 to 22 $\frac{1}{2}$	12 to 14
27 $\frac{1}{2}$ to 25	22 $\frac{1}{2}$ to 20	14 to 50
25 to 22 $\frac{1}{2}$	20 to 17 $\frac{1}{2}$	50 to 140
22 $\frac{1}{2}$ to 20	17 $\frac{1}{2}$ to 15	140 to 275
20 to 17 $\frac{1}{2}$	15 to 12 $\frac{1}{2}$	275 to 11*

* Over-vulcanized soft rubber.

portion of sulfur to rubber that will give a semi-ebonite and for accelerated cures between 15 and 17.5 parts of sulfur per 100 of rubber. An increase in the proportion of sulfur led to a progressive decrease in flexibility and increase in toughness. This relationship reached a limit with the inflexible ebonite. The best samples of semi-ebonite thus represented an optimum combination of the properties of flexibility and toughness or tensile strength.

The presence of Vulcafor Resin lowered the number of flexings before rupture.

This is consistent with the observations regarding the greater toughness of the accelerated products shown by the increase in the tensile strength. The curves in Fig. 8 suggest that a lower proportion of sulfur than 17.5 parts per 100 of rubber would give an accelerated product more flexible yet worthy of inclusion among the semi-ebonites. On similar grounds an unaccelerated product containing a little more than 25 parts of sulfur per 100 of rubber would probably yield a tougher, less flexible semi-ebonite. In Table XXVI unaccelerated and accelerated semi-ebonites

TABLE XXVII

DECREASE IN FLEXINGS BEFORE RUPTURE WITH OVEN-AGING								
Sulfur	25	25	22.5	22.5	20	20	17.5	17.5
Nonox	0	1	0	1	0	1	0	1
Aging Hours	Flexings before Rupture—Unaccelerated Product							
0	37,728	47,926	112,680	129,481	230,274	275,909	12,742	11,631
220	740	1,184	2,845	2,105	3,460	1,469	2,394	2,045
387	246	629	519	344	191	410	492	444
554	82	94	7	33	4	14	272	206
Aging Hours	Flexings before Rupture—Accelerated Product							
0	13,808	13,707	15,724	14,084	48,097	48,289	140,643	138,696
165	1,623	2,985	1,050	858	1,944	2,189	1,225	2,571
334	986	1,235	500	500	700	593	350	507
651	72	40	80	60	100	280	260	272

giving similar flexing results are compared. An attempt is made to complete the comparison by interpolation, these figures being in italics.

Table XXVI suggests that the Vulcafor Resin accelerated the cure rather more than was allowed for by the ratio of 5 to 2 in the times of cure. It reduced the amount of sulfur necessary to produce semi-ebonite by 20 to 25 per cent, yielded

TABLE XXVIII

DECREASE IN FLEXINGS BEFORE RUPTURE WITH EXPOSURE TO ULTRA-VIOLET LIGHT								
Sulfur	25	25	22.5	22.5	20	20	17.5	17.5
Nonox	0	1	0	1	0	1	0	1
Aging Hours	Flexings before Rupture—Unaccelerated Product							
0	37,728	47,926	112,680	129,481	230,274	275,909	12,742	11,631
5	22,363	31,892	94,226	111,353	201,094	227,883	7,005	8,962
10	15,860	17,160	72,547	85,737	185,072	111,600	5,984	6,528
15	10,534	11,427	42,594	59,206	116,132	125,644	2,310	1,892
Aging Hours	Flexings before Rupture—Accelerated Product							
0	13,808	13,707	15,724	14,084	48,097	48,289	140,643	138,696
5	6,109	3,260	5,513	4,615	38,448	35,227	73,234	82,103
10	5,899	2,756	2,265	1,849	29,069	16,820	45,618	45,234
15	1,768	1,352	1,991	2,868	21,496	25,017	11,670	25,027

semi-ebonite over a rather wider range than unaccelerated curing, and improved the tensile strength or toughness of the product.

The Effect of Nonox upon the Number of Flexings before Rupture.—From Table XXV and Fig. 8 it is seen that the Nonox, in the absence of Vulcafor Resin, increased the number of flexings before rupture. The effect was more pronounced as the proportion of sulfur to rubber decreased. The effect was not apparent with the accelerated product, the accelerator nullifying the effect of the antioxidant. As the flexibility is increased at the expense of toughness it may be said that, from this

point of view, the presence of Nonox tends to give a poorer semi-ebonite under the conditions of the present experiments.

The Effect of Oven-aging upon the Flexings before Rupture of Semi-Ebonites.—Each time the strips were removed from the oven to be weighed (see Part 1), one of the

TABLE XXIX
AVERAGE DECREASE IN NUMBER OF FLEXINGS BEFORE RUPTURE, WITH
EXPOSURE TO ULTRA-VIOLET LIGHT

Aging Hours	20 Parts of Sulfur per 100 of Rubber Flexings before Rupture (in Thousands)			
	Unaccelerated Cure		Accelerated Cure	
	No Nonox	With Nonox	No Nonox	With Nonox
0	126.9	151.1	54.5	53.7
5	105.9	123.7	30.8	31.3
10	91.1	71.5	20.7	16.6
15	56.4	62.1	9.2	13.6

strips was set aside for the flexing test. The results obtained are shown in Table XXVII.

One week's exposure in the oven reduced the number of flexings before rupture to relatively negligible figures, and neither Vulcafor Resin nor Nonox appeared to retard this to any appreciable extent. Some significance may be attached to the

TABLE XXX
DECREASE IN THE NUMBER OF FLEXINGS OF THE UNACCELERATED PRODUCT
WITH NATURAL AGING

Sulfur	25	25	22.5	22.5	20	20	17.5	17.5
Nonox	0	1	0	1	0	1	0	1
Sheltered Natural Aging								
Aging Hours								
0	37,728	47,926	112,680	129,481	230,274	275,909	12,742	11,631
720	27,100	36,729	75,826	126,403	211,263	210,000	10,163	9,862
1174	19,605	38,286	60,611	99,550	158,754	161,130	6,424	7,011
2736	15,188	22,375	32,096	61,446	75,000	120,160	3,808	4,623
3552	8,220	15,319	24,041	38,016	22,822	64,683	1,651	2,400
4487	1,100	3,270	5,608	9,516	43,276	47,749	2,070	1,710
Exposed Natural Aging								
Aging Hours								
0	37,728	47,926	112,680	129,481	230,274	275,909	12,742	11,631
720	14,268	21,801	36,435	76,901	191,363	261,723	9,573	7,721
1124	6,976	17,234	32,553	74,770	138,593	207,804	5,816	4,324
2736	5,130	14,058	27,887	59,276	108,460	141,323	4,481	4,457
3552	4,471	12,990	6,430	20,652	111,672	92,747	3,935	2,050
4487	1,250	2,368	4,543	3,572	75,423	66,535	1,872	1,849

fact that during this period the fall was much greater for the unaccelerated than for the accelerated products. This suggests that the accelerator may have retarded the aging.

The Effect of Exposure to Ultra-Violet Light upon the Flexings before Rupture.—Samples exposed for short periods to ultra-violet light were tested upon the flexing machine, and the results are shown in Table XXVIII.

For the purposes of easy comparison these results were summarized in Table XXIX, the unaccelerated product containing 17.5 parts of sulfur being omitted.

A considerable falling-off in the number of flexings was observed. The Nonox present apparently did not retard the aging to any appreciable extent. Though the fall in the flexings was less for the accelerated than for the unaccelerated product it is

difficult to draw conclusions from Tables XXVIII and XXIX as to the better aging product.

The results of the test show that rapid deterioration occurs when the semi-

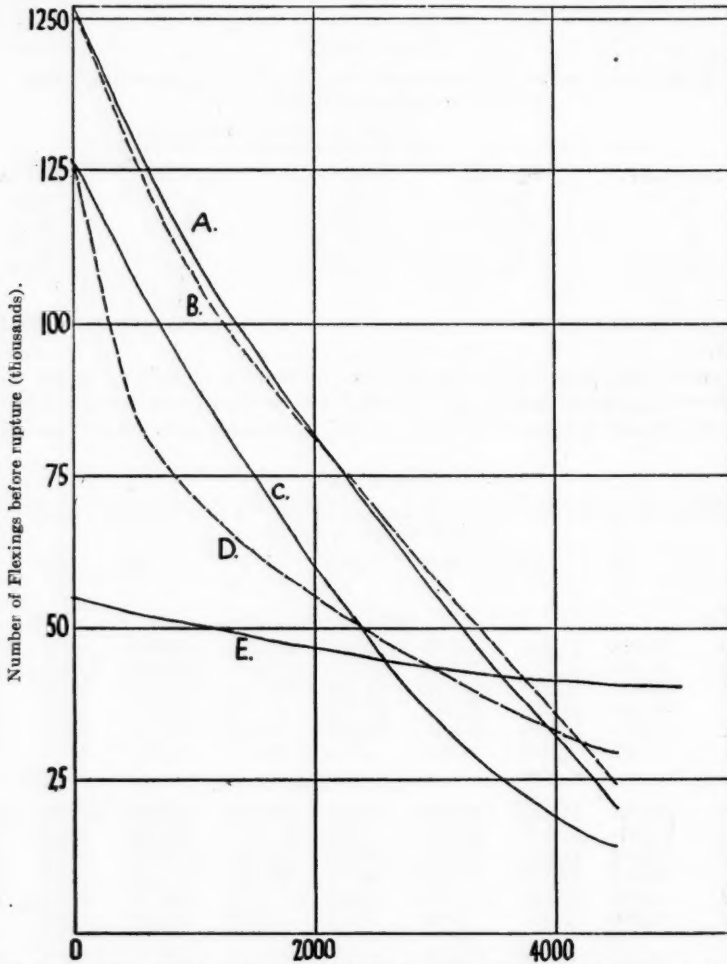


Figure 9—The Effect of Nonox and Vulcafor Resin Upon the Flexings before Rupture of Naturally Aged Semi-Ebonite

Natural aging-hours—

- A. Unaccelerated product, containing Nonox—sheltered aging
- B. Unaccelerated product, containing Nonox—exposed aging
- C. Unaccelerated product, not containing Nonox—sheltered aging
- D. Unaccelerated product, not containing Nonox—exposed aging
- E. Accelerated products. Typical curve

ebonites are exposed to ultra-violet light. Fifteen hours' exposure appears to be as effective as approximately 4 months' natural aging.

The Effect of Natural Aging upon the Number of Flexings before Rupture.—In Tables XXX and XXXI are recorded the number of flexings before rupture of unaccelerated and accelerated products, respectively, that had been aged naturally.

TABLE XXXI

DECREASE IN THE NUMBER OF FLEXINGS OF THE ACCELERATED PRODUCT
WITH NATURAL AGING

Sulfur Nonox	25 0	25 1	22.5 0	22.5 1	20 0	20 1	17.5 0	17.5 1
Aging Hours	Sheltered Natural Aging							
0	13,808	13,707	15,724	14,084	48,097	48,289	140,643	138,696
528	12,010	11,886	14,931	11,666	45,457	39,274	135,738	131,092
1153	12,567	9,440	10,862	8,184	45,223	44,901	131,636	129,892
1678	9,606	10,867	8,743	9,227	35,332	38,016	127,056	130,063
2230	10,443	9,149	9,275	8,850	34,200	32,343	128,176	126,401
2684	8,034	9,706	7,810	8,504	33,870	33,457	123,518	127,009
5062	6,591	5,814	6,022	7,100	31,686	29,026	111,198	119,681
Aging Hours	Exposed Natural Aging							
0	13,808	13,707	15,724	14,084	48,097	48,289	140,643	138,696
528	11,760	12,700	14,378	13,746	47,134	44,314	138,491	136,724
1153	12,234	11,741	15,455	14,001	42,826	39,940	134,273	130,907
1678	11,017	10,579	13,631	13,440	38,763	35,413	135,602	132,742
2230	10,549	8,599	12,082	12,391	39,412	37,846	128,049	126,026
2684	9,378	7,906	11,106	9,693	36,085	34,329	119,430	121,437
5062	8,135	4,448	8,615	10,850	32,385	30,047	107,622	114,822

TABLE XXXII

AVERAGE DECREASE IN NUMBER OF FLEXINGS BEFORE RUPTURE WITH
NATURAL AGING OF THE UNACCELERATED PRODUCTS

Aging Hours	20 Parts of Sulfur per 100 of Rubber Flexings before Rupture (in Thousands)			
	Sheltered Aging		Exposed Aging	
	No Nonox	With Nonox	No Nonox	With Nonox
0	126.9	151.1	126.9	151.1
720	104.7	124.4	80.7	120.1
1174	79.7	99.7	59.4	99.9
2736	40.8	68.0	47.2	71.6
3552	18.3	39.3	40.9	42.1
4487	16.7	20.2	27.1	24.2

TABLE XXXIII

AVERAGE DECREASE IN NUMBER OF FLEXINGS BEFORE RUPTURE WITH
NATURAL AGING OF THE ACCELERATED PRODUCT

Aging Hours	20 Parts of Sulfur per 100 of Rubber Flexings before Rupture (in Thousands)			
	Sheltered Aging		Exposed Aging	
	No Nonox	With Nonox	No Nonox	With Nonox
0	54.5	53.7	54.5	53.7
528	52.0	48.5	52.9	51.8
1153	50.1	48.1	51.2	49.1
1678	45.2	47.1	49.7	48.0
2230	45.5	44.2	47.5	46.2
2684	43.3	44.7	44.0	43.3
5062	38.9	40.4	39.2	40.0

For the purpose of easy comparison the results of 208 tests are summarized in Tables XXXII and XXXIII and Fig. 9. The unaccelerated product containing 17.5 parts of sulfur has been omitted.

The flexing test suggests that the semi-ebonites aged reasonably well. The accelerated products were far better in this respect, for over six months' aging the number of flexings fell to approximately 75 per cent of the original value, while the

unaccelerated product fell to only 16 per cent (see Tables XXXII and XXXIII). The Vulcafor Resin thus retarded the aging very considerably. Table XXXIII shows that the Nonox, in the presence of Vulcafor Resin, had little effect in retarding the fall in the number of flexings with natural aging. With the unaccelerated products the Nonox had little or no effect.

Stress-Strain Tests.—Both the Scott and Schopper machine tests were abandoned in the first instance, for reasons given in Part 1. It was considered later, however,

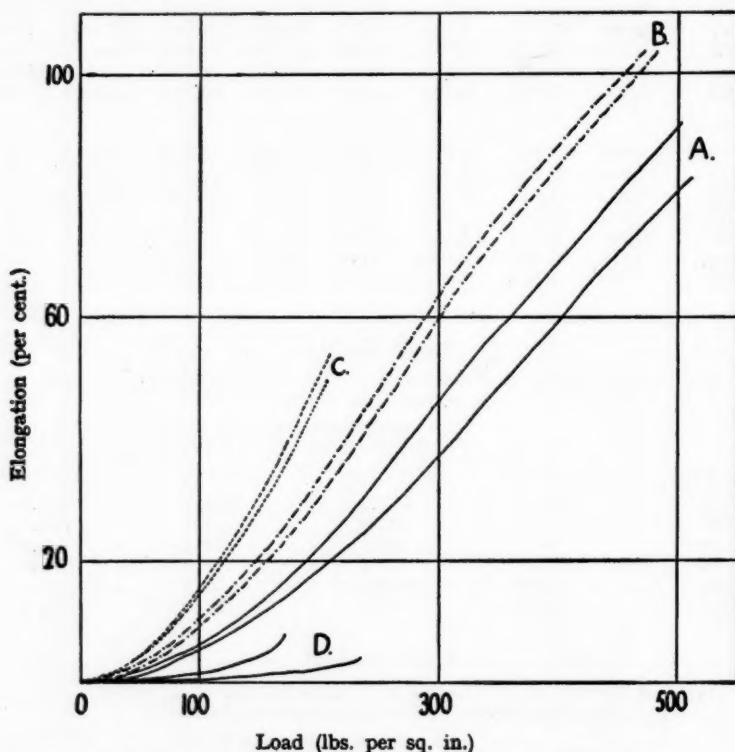


Figure 10—Stress-Strain Curves for Unaccelerated Semi-Ebonites

- A. Products containing 25 parts of sulfur per 100 of rubber
 - B. Products containing 22.5 parts of sulfur per 100 of rubber
 - C. Products containing 20 parts of sulfur per 100 of rubber
 - D. Products containing 17.5 parts of sulfur per 100 of rubber
- In each case except D product not containing Nonox is nearer the load axis

that, using the test-piece standard to this work, some comparison with a genuine leather substitute would be possible by means of the Scott machine.

The test-piece was clamped in the apparatus in such a way that the pierced end was free from strain. The edge of the hole was placed flush with the edge of the grips. Parallel lines, 2 or 3 inches apart, were drawn in ink across the test-piece and the jaws of the apparatus moved apart at the rate of approximately 1.6 inches per minute. Observations of the load, automatically recorded on a dial, were made for equal small elongations, shown by a ruler held lightly against the specimen. The loads given by the machine, adjusted to give correct readings upon an area of 0.1

TABLE XXXIV
STRESS-STRAIN VALUES FOR UNACCELERATED PRODUCTS

Sulfur Nonox	25 0	25 1	22.5 0	22.5 1	20 0	20 1	17.5 0	17.5 1
Percentage Elongation	Load in Lbs. per Sq. Inch							
4.2	85	75	75	70	55	50	160	235
8.3	130	110	105	90	80	75	170	
12.5	160	140	125	115	95	90		
16.7	190	160	145	135	115	105		
20.8	215	180	165	150	125	120		
25.0	235	205	180	160	140	130		
29.2	255	220	195	180	155	145		
33.3	280	235	205	200	165	160		
37.5	300	260	220	210	175	170		
41.7	315	280	235	225	190	185		
45.8	340	300	250	240	200	195		
50.0	360	315	260	255	205	200		
54.2	380	325	275	265		210		
58.3	395	345	295	285				
67.5	415	360	315	300				
66.7	440	380	325	315				
70.8	460	395	340	335				
75.0	475	415	350	345				
79.2	495	435	370	365				
83.3	510	455	380	380				
87.5		480	400	395				
91.7		500	425	415				
95.8			445	435				
100			460	455				
104.2			480	470				

TABLE XXXV
STRESS-STRAIN VALUES FOR ACCELERATED PRODUCTS

Sulfur Nonox	25 0	25 1	22.5 0	22.5 1	20 0	20 1	17.5 0	17.5 1
Percentage Elongation	Load in Lbs. per Sq. Inch							
8	176	165	158	124	102	90	70	60
16	254	237	224	186	144	132	108	108
24	310	288	274	235	172	165	140	130
32	360	338	315	276	210	195	161	155
40	395	371	357	317	234	220	192	173
48	436	418	398	359	258	250	208	191
56	478	453	431	386	300	270	235	220
64	517	495	464	428	330	300	253	237
72	560	537	514	463	358	330	280	255
80	604	575	539	497	382	355	288	264
88	646	618	573	524	408	375	311	297
96	692	655	614	566	432	400	333	306
104	730	699	647	600	450	430	346	323
112	775	738	688	642	474	450	365	348
120	820	782	722	676	498	465	387	361
128	864	829	771	724	516	486	405	384
136	910	875	813	766		500		396
144	960	920	863	814		517		407
152	1014	972	905	862				
160	1068	1022	962	911				
168	1128	1084	1013	972				
176	1192	1150	1079	1035				
184	1264	1220	1145.4	1100				
192		1296		1167				
200		1364		1228				

square inch, were multiplied by the appropriate factor to give the loads in lbs. per sq. in. of the specimen under test.

Experimental Results.—Typical results of the Scott machine test upon the unaccelerated and accelerated products are shown in Tables XXXIV and XXXV, and graphically in Figs. 10 and 11, respectively.

The unaccelerated product containing 17.5 parts of sulfur per 100 of rubber was

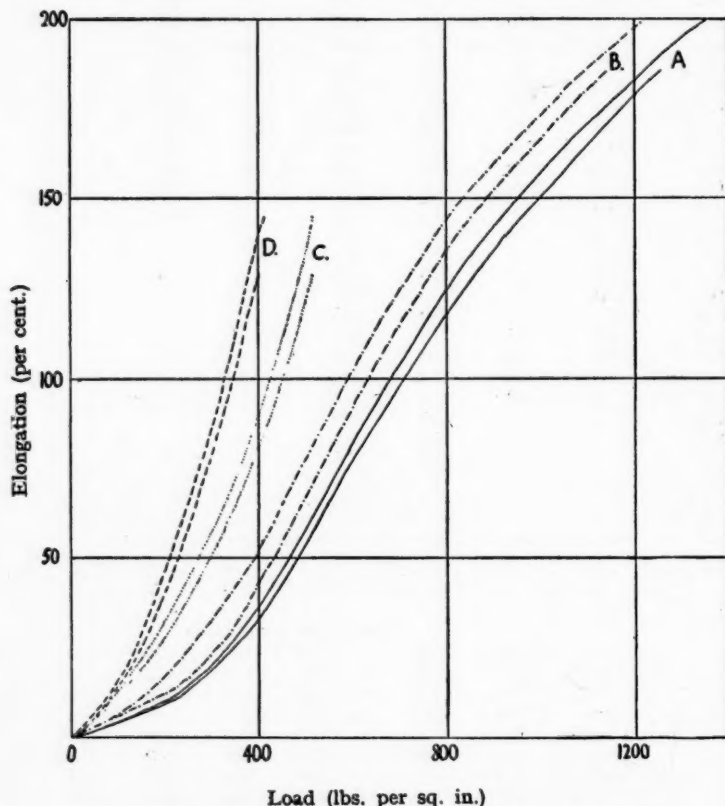


Figure 11—Stress-Strain Curves for Accelerated Semi-Ebonites

- A. Products containing 25 parts of sulfur per 100 of rubber
 - B. Products containing 22.5 parts of sulfur per 100 of rubber
 - C. Products containing 20 parts of sulfur per 100 of rubber
 - D. Products containing 17.5 parts of sulfur per 100 of rubber
- In each case product not containing Nonox is nearer the load axis

typical of the highly over-vulcanized soft rubbers in that it snapped short under a relatively high load for a small elongation. The rest of the products investigated showed reasonably high tensile strength and percentage elongation. For the purposes of easy comparison a summary is shown in Table XXXVI of the tensile strengths and tensile products of the different samples.

Consideration of the results summarized in Table XXXVI and the Figs. 10 and 11, led to the following conclusions:

An increase in the proportion of sulfur within the limits employed in this investi-

gation yielded products of increasing toughness and percentage elongation at break. An optimum combination of the properties of toughness and elasticity appeared to be reached with products intermediate between the semi-ebonites containing 22.5 and 25 parts of sulfur per 100 of rubber. The lowest proportion of sulfur that yielded a semi-ebonite product lay between 17.5 and 20 parts per 100 of rubber with unaccelerated vulcanization and appreciably less than this with accelerated vulcanization.

The presence of Vulcafor resin yielded products of far greater toughness and percentage elongation at break. Acceleration of the cure improved the product in

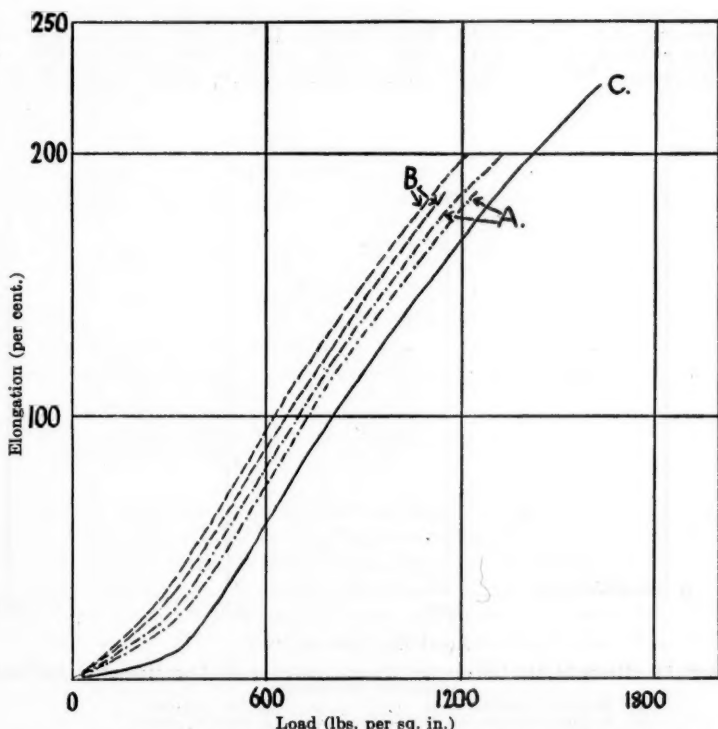


Figure 12—Stress-Strain Curves of a Vulcanized Soling Compound and Accelerated Semi-Ebonites

- A. Semi-ebonite containing 25 parts of sulfur per 100 of rubber
- B. Semi-ebonite containing 22.5 parts of sulfur per 100 of rubber
- C. Vulcanized soling mix

every way and encouraged the belief that such a product would compare reasonably with the highly compounded vulcanized rubber widely used for footwear.

The presence of an antioxidant, Nonox, slightly impaired the toughness of the material, yielding stress-strain curves slightly nearer the elongation axis. In all but one case a somewhat greater percentage elongation was obtained.

Comparison between the Toughest Semi-Ebonites and a Black Soling Compound.—The following mix was prepared: rubber, 100 parts; mineral rubber, 5; carbon

TABLE XXXVI

TENSILE STRENGTH, PERCENTAGE ELONGATION AND TENSILE PRODUCT OF THE SEMI-EBONITES INVESTIGATED

Sulfur	25	25	22.5	22.5	20	20	17.5	17.5
Nonox	0	1	0	1	0	1	0	1
Unaccelerated Product								
Tensile strength (lbs. per sq. in.)	510	500	480	470	205	210	170	235
Elongation at break %	83.3	91.7	104.2	104.2	50.0	54.2	8.3	4.2
Tensile product $\div 10^3$	42.5	45.9	50.0	49.0	10.3	11.40	1.4	1.1
Accelerated Product								
Tensile strength (lbs. per sq. in.)	1264	1364	1145	1228	516	517	405	407
Elongation at break %	184	200	184	200	128	144	128	144
Tensile product $\div 10^3$	232.6	272.8	210.8	245.6	66.0	74.4	51.8	58.6

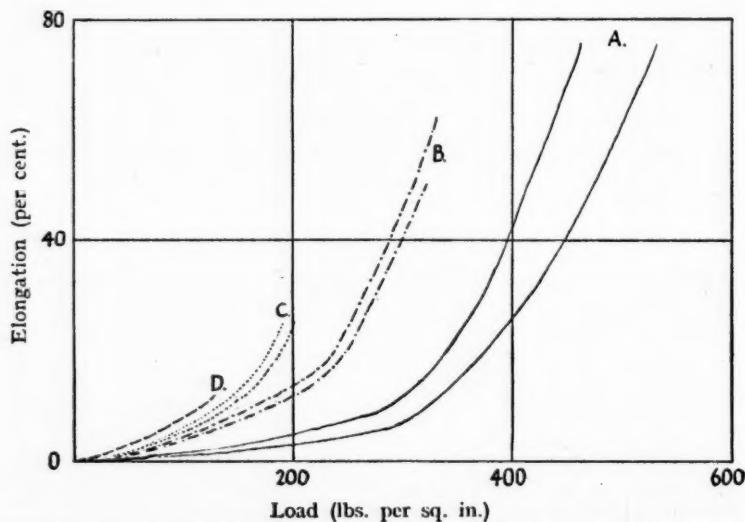


Figure 13—Stress-Strain Curves for Unaccelerated Semi-Ebonites after Natural Aging for 4487 Hours

- A. Products containing 25 parts of sulfur per 100 of rubber
 B. Products containing 22.5 parts of sulfur per 100 of rubber
 C. Products containing 20 parts of sulfur per 100 of rubber
 D. Products containing 17.5 parts of sulfur per 100 of rubber
 In each case product not containing Nonox is nearer the load axis

TABLE XXXVII

TYPICAL STRESS-STRAIN VALUES FOR THE BLACK SOLING COMPOUND

Per cent elonga- tion	12.5	25	37.5	50	62.5	75	87.5	100	112.5
Load, lbs. per sq. in.	333	415	490	545	600	660	720	788	856
Per cent long- ation	125	137.5	150	162.5	175	187.5	200	212.5	225
Load, lbs. per sq. in.	938	1000	1087	1128	1220	1305	1420	1520	1624

black, 120; stearic acid, 1; zinc oxide, 5; pine tar, 2; sulfur, 4; and diphenylguanine, 2 parts. The mix was cured for thirty minutes at a steam pressure of 50 lbs. per square inch.

A typical result of the Scott machine test upon the vulcanized product is shown in Table XXXVII, and is compared graphically with the accelerated semi-ebonites containing 22.5 and 25 parts of sulfur per 100 of rubber in Fig. 12. The curves were similar to one another even to the slight bending away from the elongation axis just prior to rupture. This appeared to be some indication of the cohesive forces in play in the rubber, the less tough specimens failing to reveal this late increase in the load before rupture. Though the black soling compound was shown to be appreciably tougher and capable of undergoing greater strain, the comparison showed that the best semi-ebonites were really good products.

The Effect of Natural Aging upon the Tensile Strength of the Unaccelerated Semi-Ebonites.—The results obtained with the Scott machine upon some samples that had been aged naturally for 4487 hours are summarized in Table XXXVIII and Fig. 13.

TABLE XXXVIII
STRESS-STRAIN VALUES FOR UNACCELERATED PRODUCTS AGED NATURALLY FOR 4487 HOURS

Sulfur Nonox	25 0	25 1	22.5 0	22.5 1	20 0	20 1	17.5 0	17.5 1
Percentage Elongation	Load in Lbs. per Sq. Inch							
12.5	340	300	210	200	150	160	130	130
25	400	350	260	250	190	200		
37.5	440	380	290	280				
50	480	417	320	310				
62.5	510	440		330				
75	530	460						

Comparison with the curves for the corresponding unaged samples in Fig. 10 shows that the material had become much tougher, but after the initial rapid increase in the load there was a relatively rapid increase in the elongation. The aging process appeared to give rise to a harder, less elastic product. The formation of an inert oxidized film at the surface, in part, explained this hardening of the semi-ebonite with aging. The percentage elongation was less in each case, the product containing 25 parts of sulfur being the least affected and reasonably resistant to aging. The Nonox had no apparent effect in retarding the aging.

The Permanent Set Observed after the Scott Machine Tests.—At the end of these tests the broken specimens were carefully pieced together. It was observed that the specimens showed a somewhat sluggish recovery after stress, but within one-half an hour had returned to within one per cent of their original length.

The authors desire to express their thanks to T. J. Drakeley for the valuable help received during the course of the investigation and the preparation of the paper for publication.

Internal Protective Coatings for Latex Containers

Investigations of Internal Protective Coatings for Latex Containers and Their Value in Minimizing Discoloration in Preserved Latex

Edgar Rhodes and K. C. Sekar

Introduction

In a previous publication (cf. *J. Rubber Res. Inst. Malaya*, 5, 176 (1934); *RUBBER CHEM. AND TECH.*, 7, 433(1934) the present authors have discussed fully the causes of discoloration in preserved latex and have shown that the iron drum which is in common use as a latex-shipment vessel is in itself a predisposing factor in the discoloration of latex. Users do not however look with favor on the substitution of a non-metallic container for the steel drum, and since suitable alternative metallic containers are prohibitive in cost, there remains little alternative but to endeavor, by the internal application of some protective medium, to reduce to a minimum the objectionable effects of the iron drum on its contents.

Since discoloration is due to the formation of dark-colored colloidal and amorphous sulfides of iron, a satisfactory drum-coating medium should prevent contact of the latex with the iron of the drum, and also if possible react with any sulfur compounds which may be liberated in the latex, to form sulfides which are either white in color or so nearly white that when present in latex they are not detectable by the eye.

It is essential that the coating should not be so brittle as to crack or flake away from the metal when drums are roughly handled in transit. If flaking occurs, serious contamination of the latex may result. The requirement is a tough, elastic film which will adhere well to the metal and which will not be appreciably affected by long contact with ammoniated latex, except in so far as it may combine with sulfur compounds to produce a white product.

The present paper describes tests which have been made on a great variety of paint-like preparations, some of which were proprietary and others of which were compounded in the laboratory.

In testing the various preparations, the fact has been kept in mind, that in the majority of cases, the preparation must be applied to the inside of an already-assembled drum having at most two small apertures. This implies that preparations which are normally slow to dry and harden do not commend themselves, because the drying time in the interior of a drum is necessarily longer than in freely circulating air. Further, the only method of application available to most estates is that of pouring an excess of the preparation into the drum, rolling, turning end over end, and finally running off the excess material. The construction of most drums does not lend itself to easy and complete drainage, so that the only readily available method of application must be considered wasteful as well as troublesome. This fact suggests in turn that suitable materials should be such as are effective in a single application or coat. In all cases therefore tests have been confined deliberately to metal carrying one coat only of any given preparation.

EXPERIMENTAL

Method of Testing

The laboratory technic adopted for testing the suitability of the various media was empirical and was based largely upon the investigations which were made in connection with the earlier investigation (*loc cit.*) into the causes of discoloration.

Strips of metal cut from an ordinary latex drum were given one coat of the material to be tested, by dipping and allowing to drain. After drying by exposure to free air for 24 hours at laboratory temperature, they were taken for test, or if not reasonably dry they were recorded as probably unsuitable. In the course of all tests, unpainted strips were used as controls for purposes of comparison.

Two tests, which in practice were found to differ in severity, were applied to each material. These were:

Test (i)—The Simple Immersion and Storage Test and

Test (ii)—Test by Partial Putrefaction Prior to Ammoniation and Storage.

The details of each test follow:

Test (i)—The Simple Immersion and Storage Test

In this test coated strips and their uncoated controls were immersed to within one-half inch of their length in latex which had been ammoniated to approximately 1 per cent NH_3 while still in a fresh condition. They were then stored for a period of six weeks, during which periodical observation of the degree of discoloration of the latex was made. The period of six weeks was chosen as being the approximate and reasonable period of time which might elapse between despatch from the estate and examination by the buyer at destination.

Test (ii)—Test by Partial Putrefaction Prior to Ammoniation and Storage

This test is much more drastic than the simple immersion test, and under it many coating media, which appeared fairly satisfactory under the conditions of the first test, permitted the induction of considerable discoloration in the latex and accordingly came under suspicion. The technic consisted in immersing the coated and uncoated strips in fresh latex containing no preservative, and allowing the whole to stand for a period of four hours before adding ammonia as preservative. During this initial four-hour period prior to ammoniation some incipient putrefaction occurs in the latex and the products of this biological activity have a particularly severe action on iron. After having ammoniated the latex to approximately 1 per cent NH_3 , it was stored for six weeks in contact with the metal strip, color observations being made as in Test (i).

In both tests, at the end of the storage period and after final color observations had been made on the latex, the strips were removed, washed with water and the condition of the filming material appraised. Media which under both tests prevented latex discoloration and which in addition were present as a hard, continuous but not brittle film at the end of the storage period were judged satisfactory; where very slight discoloration occurred in the latex, the medium was classified as imperfect, and where appreciable discoloration was apparent, as unsatisfactory. The unsatisfactory media showed in practically every case appreciable softening and/or loosening of the film at the end of the storage period.

Proprietary Materials Tested

It was at first considered likely that, among the proprietary brands of paints and protective solutions which were available in Malaya and which could be obtained

from Europe, some would be found which combined cheapness with efficiency, and examination of a number of proprietary materials of different general types was made. In most cases the manufacturers were pre-informed of the requirements and supplied media which were expected to be satisfactory. The results of the examination of these materials are summarized in Table I.

TABLE I

Key No. of Paint	Type of Base	Observations on Drying Rate	Condition of Film after Six Weeks' Storage of Painted Strip in Latex	Suitability of Paint as Judged by De- gree of Discolora- tion in Tests (i) and (ii)	General Remarks
1	Bituminous	Rather slow	Unsatisfactory	Unsuitable
2	Bituminous	Satisfactory	Continuous Soft	Unsatisfactory	Unsuitable
3	Bituminous	Satisfactory	Continuous. Soft	Unsatisfactory	Unsuitable
4	Bituminous	Rather slow	Continuous. Soft	Unsatisfactory	Unsuitable
5	Bituminous	Rather slow	Continuous. Soft	Unsatisfactory	Unsuitable
6	Bituminous	Too slow	Continuous. Soft	Imperfect	Unsuitable because of slow drying
7	Bituminous	Too slow	Unsatisfactory	Unsuitable
8	Pigment, in oil vehicle	Satisfactory	Softened. Fell away	Satisfactory	Unsuitable because film leaves metal
9	Chlorinated Naphthalene	Satisfactory	Continuous. Hard	Imperfect	Fairly satis- factory
10	Chlorinated Rubber	Satisfactory	Continuous. Hard	Satisfactory	Suitable
11	Soluble Bakelite	Satisfactory	Continuous. Soft	Unsatisfactory	Unsuitable
12	Soluble Bakelite	Satisfactory	Continuous. Fairly hard	Unsatisfactory	Unsuitable
13	Soluble Bakelite	Satisfactory	Continuous. Hard	Imperfect	Fairly satis- factory
14	Not known	Satisfactory	Softened. Fell away	Unsatisfactory	Unsuitable
15	Not known	Satisfactory	Softened. Fell away	Unsatisfactory	Unsuitable
16	Not known	Satisfactory	Continuous. Soft	Imperfect	Unsuitable. Film too soft
17	Not known	Satisfactory	Continuous. Fairly hard	Unsatisfactory	Unsuitable
18	Not known	Satisfactory	Continuous. Soft	Unsatisfactory	Unsuitable
19	Not known	Satisfactory	Continuous. Soft	Imperfect	Unsuitable. Film too soft
20	Not known	Satisfactory	Fell away	Unsatisfactory	Unsuitable
21	Not known	Satisfactory	Film breaking	Unsatisfactory	Unsuitable
22	Rubber derivative	Satisfactory	Continuous. Hard	Unsatisfactory	Unsuitable
23	Rubber derivative	Satisfactory	Continuous. Soft	Unsatisfactory	Unsuitable
24	Rubber derivative	Satisfactory	Continuous. Hard	Imperfect	Fairly satis- factory
25	Not known	Satisfactory	Continuous. Soft	Unsatisfactory	Unsuitable

The tests on the proprietary materials indicated that the only really satisfactory material was preparation No. 10, the base of which consisted of chlorinated rubber. In addition, preparation No. 9 containing chlorinated naphthalene showed promise together with No. 24, which is in the main a derivative of rubber, and No. 13 which is a patented and rather expensive preparation of soluble Bakelite. Chlorinated rubber and chlorinated naphthalenes are obtainable on the open market and this fact prompted further tests with media compounded in the laboratory from these bases.

Laboratory-Compounded Preparations from Proprietary Bases

Twelve different mixtures containing the chlorinated rubber "Pergut" with suitable solvents, softeners, and plasticizers in different proportions were subjected to the tests, and all gave very satisfactory results. It was felt, however, that the process of compounding would be too difficult for the average estate and that the cost would be too great.

Twenty-three preparations containing chlorinated naphthalenes and mixtures of these substances with bituminous substances as softeners were prepared and tested. They were deemed to be unsuitable on grounds of difficulty of preparation and application. Many were in any case unsuitable because they permitted the induction of discoloration.

At this stage in the investigation the only reasonably satisfactory material which could be obtained in Malaya was the soluble Bakelite preparation (No. 13) which is sold under the name of "Tropelite Black." This material has since been tested on a larger scale in large bulking tanks and trial drum shipments, and, though not perfect, is nevertheless effective in minimizing though not preventing discoloration. It is, however, too expensive for general adoption. The proprietary preparations Nos. 9, 10, and 24 were not and still are not available in Malaya.

The materials tested up to this stage had without exception been of the type which might protect iron from contact with latex, but they were not compounded of substances which could readily react with any active sulfur compounds which might be produced in the latex. Since so little success had attended trials with the simple protective media, attention was turned to the production of a reactant filming medium. The aim was to produce a film containing a chemical substance which would react preferentially with latex-sulfur compounds to produce a white sulfide rather than the black iron sulfide. Zinc oxide at once suggested itself as a suitable and cheap substance, and laboratory tests were made with filming media containing zinc oxide as the essential principle.

Preparations Containing Zinc Oxide

(a) *Zinc Oxide in an Oil Vehicle.*—Metal strips treated with paints in which zinc oxide was dispersed in an oil vehicle proved unsuitable. Latex discoloration did not occur, but the film softened, fell away from the metal and contaminated the latex with its oily vehicle. The failure was judged to be due to an incorrect choice of vehicle.

(b) *Zinc Oxide in Rubber Solutions.*—Solutions of rubber in an organic solvent were used as a vehicle for zinc oxide. They gave zinc oxide films which adhered well to metal and which prevented latex discoloration. Rubber solutions are troublesome and expensive to prepare on estates, and the obvious substitute was latex itself.

(c) *Zinc Oxide-Latex Films.*—A number of zinc oxide-latex films containing

different proportions of zinc oxide and ammoniated latex were tested. Very good results were obtained with these films. It remained to choose a mixture in which the proportion of zinc oxide was high enough to prevent discoloration but not so high that the deposited film of rubber and zinc oxide would be hard, lacking in adhesive power and likely to strip away from the metal. It was found that for best results the filming medium should contain approximately 20 per cent by weight of zinc oxide, calculated on the weight of the ammoniated latex vehicles. In laboratory tests this filming medium gave consistently satisfactory results, and near the end of 1934 instructions for the use of this medium were first issued to an estate. The instructions are:

"Mix 2 lbs. of zinc oxide to an extremely smooth paste with one quart of water. Mix this paste very thoroughly with one gallon of ammoniated latex containing 0.7 per cent ammonia. The mixture is now ready for use as a filming medium.

"It is inadvisable to prepare more of the complete filming agent than will suffice for one day's supply of latex. A week's supply of the zinc oxide-water paste can, however, be prepared without danger. This should be thoroughly stirred before drawing the daily supply for admixture with the ammoniated latex vehicle. Before application, the filming mixture should be thoroughly stirred because the zinc oxide tends to settle out. Filming is carried out by pouring an excess of the mixture into a clean drum, rolling, and turning end over end, so as to film all internal surfaces. The excess filming agent is then drained out and the drum is exposed to the sun to dry the internal film. When the film is dry the drum is then ready for filling with ammoniated latex."

Where second-hand oil drums are used, it is important that drums which have been cleaned should be filmed within a few hours. Rust spots rapidly develop on the inside of wet, oil-free drums. If rust spots are present, the applied film may be unsatisfactory because either the rust spots may not be completely covered, or the film, if continuous, may not adhere firmly to the metal.

Large-Scale Latex Shipment Trials with Drums Filmed with Latex-Zinc Oxide Medium

Large-scale latex shipment trials of several thousand gallons in latex-zinc oxide filmed drums were made early in 1935 by J. S. Laird, the Manager of Jemima Estate. These shipments were made on the basis of the laboratory tests described above, and the customary cautious but time-consuming intermediate stages of small-scale trial shipments were thereby eliminated. Our thanks are due to him for the confidence which he showed and which proved fortunately not to be misplaced. J. B. Crockett, President of Heveatex Corporation, Melrose, Mass., who in the fact of being willing to accept and report to us fully on latex from such consignments, rendered an equally great service.

A number of large-scale consignments have demonstrated that when the latex-zinc oxide filming medium is carefully applied, latex may be expected to arrive at destination in a good white condition. The film itself adheres well to the metal and cases of film-stripping in transit are few. These trials have demonstrated adequately the effectiveness of the film against discoloration caused by the metal container.

The trials have also demonstrated that the film possesses one disadvantage in that it tends to reduce the stability of the latex. We are advised, however, that if the buyer is previously made aware of the fact that drums have been filmed, he can in nearly all cases correct this reduction in stability without serious difficulty.

DISCUSSION

The work on latex drum-filming media is a natural corollary to the earlier investigations (1) on the causes of latex discoloration. The effectiveness of the latex-zinc oxide medium which was developed after many fruitless tests on proprietary protectives, provides in itself a confirmation of the correctness of the original postulate that latex discoloration is due to the formation of amorphous and colloidal iron sulfide within the latex. The substitution of zinc for iron as the reactant metal should, if the postulate be correct, result in the formation of white and therefore to the eye undetectable sulfides. Such has proved to be the case. British Patent No. 434,214 of the Metallgesellschaft Aktiengesellschaft provides for the addition of free zinc oxide to preserved latex itself in order to prevent discoloration. In our treatment of the problem such a procedure was considered undesirable and was purposely avoided. The chief reason was that users might object to the deliberate addition of free powders such as this to latex before shipment. In the latex-zinc oxide films described, the zinc oxide present is held in a rubber matrix and is not free to enter the body of the latex. Further, the product of its reaction with the sulfur bodies of the latex, namely zinc sulfide, must itself remain to a large extent bound in that matrix. It is considered that the latex-zinc oxide film has the effect of preventing discoloration while giving rise to the minimum of what might be termed contamination.

It has been observed that the latex-zinc oxide films tend to reduce stability. This might have been expected but it is difficult to envisage how it can be avoided. The reduction in stability is almost certainly due to the formation of traces of soluble ammonium zincate by the action of ammonia on the zinc oxide film. The traces of zinc salt thus brought into solution would naturally tend to reduce stability.

It is pointed out that the latex-zinc oxide film has not been tested by us in shipment trials with centrifugally concentrated latex. Because the filming is known to reduce stability, it is possible that where the dry rubber content is of the order of 60 per cent, and where the concentrate is not heavily stabilized but preserved solely with ammonia, the reduction in stability may have more serious effects than are found with preserved field latex.

Similar remarks would apply but probably to a lesser degree in the case of gum-creamed latex. Producers of centrifugal and gum-creamed latex are therefore advised to proceed with caution in the use of the latex-zinc oxide drum-film and to make small trial shipments before attempting bulk consignments. It is also the fact that high natural stability in preserved normal latex is considered essential by a few users, and producers of such latex are advised wherever possible to consult the user before commencing the practice of filming with the latex-zinc oxide medium.

A Rapid Method for Determining Sulfur and Ash in Rubber by Ignition of the Rubber in Oxygen

B. Kreps

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A large number of investigators have studied the problem of a rapid and accurate determination of total sulfur in rubber, but have been confronted by the difficulties of selecting a rapidly oxidizing mixture without the danger of explosion.¹

Of the many dry and wet methods of oxidizing sulfur in rubber, that of Henriques² is considered the best. This method, known to rubber technologists, consists in oxidizing rubber with strong nitric acid and fusing the product with a mixture of sodium carbonate and potassium nitrate. This method, however, is inconvenient, complicated and lengthy (three days).

This situation prompted the authors to search for a new and more rapid method.

The determination of sulfur by ignition of rubber in a glass tube in a current of oxygen results in complete oxidation of the total sulfur in the rubber, including the free, organically combined and sulfite-soluble sulfur. The sulfur dioxide formed is carried over by the current of oxygen into a receiver, containing hydrogen peroxide, and is oxidized completely to sulfuric acid. Any sulfates contained in the rubber, such as barytes and gypsum (very seldom), remain unchanged in the ash.

In pure rubber mixtures, or in mixtures containing ingredients incapable of forming sulfates (antimony sulfide), all of the sulfur passes completely into the receiver. Zinc oxide and magnesium oxide are partly converted to sulfates. Thus rubber containing 4 per cent of ZnO and 2.5 per cent of total sulfur gave an ash containing 0.11 and 0.13 per cent sulfur in two parallel determinations. In the analysis of rubber containing 40 per cent of whiting, the resulting ash contained one-third of the sulfur as CaSO₄. The formation of sulfates, however, does not affect the accuracy of the method, but only retards the work by 10-15 min. After preliminary experiments with simple mixtures, the effectiveness of the proposed method was checked with highly complex rubber mixtures.

FORMULA OF RED RUBBER

		%
Smoked sheet	100	or 36.7
Whiting	103	or 38
Antimony trisulfide	3	or 1.1
Sulfur	1.5	or 0.55
Factice	10	or 3.67
Petrolatum jelly	4.5	or 1.65
Antimony pentasulfide	20	or 7.34
Lithopone	38	or 11
	272	or 100

Experiments confirmed the theoretical postulation that in this case all the sulfur, except that in barytes, is oxidized to sulfur dioxide, a part of which escapes into the receiver and another part of which reacts with the ash oxides and whiting.

Experimental Part

1. *Arrangement of the Apparatus.*—A combustion tube 40–50 cm. long and 20–22 mm. inside diam. is held in a horizontal position by means of an iron support.

Experiments showed that the reaction proceeds poorly in small tubing because of insufficient oxygen. One end of the tubing is connected with the source of oxygen. The oxygen is dried by passing it into a Tishchenko flask containing concentrated sulfuric acid (chemically pure). At the opposite end the tubing is connected with two communicating Drechsel flasks, the first of which is charged with 5 to 30 cc. of 2 per cent hydrogen peroxide depending on the supposed content of sulfur in the rubber, and the second flask with one-half of this amount. It is better to use perhydrol, which must be tested for its sulfuric acid content, and a corresponding correction for H_2SO_4 must be introduced in the calculation of the results of the determination of sulfur in rubber. The flasks are filled three-quarters full of water (the receiver should be tested for air tightness). When the assembly is ready for use, a boat, 7–8 cm. long, charged with the finely cut rubber sample, is placed in the tubing somewhere near the center section. The tubing must be fastened by the support clamp at the end connected with the oxygen supply. In the small tube connecting the combustion tubing and the receiver is placed a piece of cotton wool to retain acid.

2. *Combustion.*—After the tubing and the receiver are connected, a current of oxygen is conducted at such a rate that single bubbles can be counted in the receiver. After the oxygen is conducted for one-half minute to displace the air, the heating of the tubing is begun with burners manipulated by hand. With one burner the tubing is heated up to the point where the boat is located, and with the other burner where the space occupied by the boat ends. The stoppers must be kept cold. After about 1 min. of heating of the tube, the heat is concentrated at the position of the boat. If the tubing becomes red-hot, the burner is moved along the tubing to prevent melting of the glass. It is advisable that the entire circumference of the tubing should be surrounded by the flame of the burner. The rubber in the boat first melts and then flames up, frequently with a shock. In this case the heating must be moderated by removing the burner. The ignition is continued until the ash becomes white, which usually consumes 4–6 minutes, depending on the composition of the rubber and the size of the sample. In most cases the soot is not burned and is deposited on the walls of the tubing. When the ash becomes white, the heating is discontinued and the connection with the oxygen supply is removed. It is not necessary to continue the ignition until all soot and softeners are burned.

3. *Operations after Ignition.*—The receiver contains sulfur in the form of H_2SO_4 . Another part of the sulfur may be contained in the ash. The ash is determined by the difference in weight of the boat with and without the ash, and the results calculated on the weight of the sample in percentage. If the walls of the boat are covered with soot, the boat is ignited in a free flame for about 2 minutes. After the boat is weighed, the determination of sulfur begins. The boat with the ash is transferred to a porcelain dish, the contents are treated with 100 cc. of water and a few drops of hydrochloric acid. If the ash is fused and adheres to the boat, it is scraped off (this happens with rubbers containing antimony). The solution is boiled, filtered, and united with the solution contained in the receiver. The mixture is boiled 5 minutes to free it from excess of hydrogen peroxide and carbon dioxide, and the boiling solution is treated with 5 cc. of HCl , and dropwise with a hot solution of barium chloride as usual. Since by this method no precipitation of silica is necessary, as is the case with the fusion method, the determination can be made in one

day. By this method of ignition some acid products of incomplete combustion pass into the receiver; hence the resulting sulfuric acid cannot be determined by acidimetric titration. The introduction of platinized asbestos with 7 per cent platinum failed to effect a complete combustion to carbon dioxide.

Analysis of Red Rubber

A rubber mixture of the same composition was used. The determination was performed by three methods: ignition in a current of oxygen, fusion, and oxidation with potassium chlorate.

Ignition was continued for 5-6 minutes, giving a completely white, clinkered ash. The analytical results are given in Table I. The sulfur in barytes was theoretically calculated, for this was necessary to know for a comparison of the resulting values. With this method, the barytes sulfur can be ordinarily disregarded. Table I

TABLE I

Expt.	Sample	% Sulfur	% Sulfur in Baryte	% Total Sulfur	Remarks
1	0.72	5.4	1.12	6.52	Ignition in oxygen and volumetric determination of sulfate
2	0.72	5.51	1.12	6.63	
3	0.72	5.5	1.12	6.62	
4	0.346	5.63	1.12	6.75	Ignition in oxygen and gravimetric determination of sulfate
5	0.201	5.68	1.12	6.8	
6	0.2379	5.67	1.12	6.79	
7	0.302	6.83	Fusion
8	0.5	6.6	
9	0.2927	6.83	
10	0.5	6.81	
11	0.5	5.9	Oxidation with potassium chlorate
12	0.5	5.9	

shows that the determination by this new method of even such a complex rubber mixture (Experiments 4, 5, and 6) gives results as accurate as those by the time-consuming method of fusion. The analysis of motor truck solid tires by the new method gave 16 per cent and by the fusion method 16.3 per cent of sulfur. A rubber-boot sample, containing a large proportion of whiting and 0.99 per cent sulfur, analyzed by the new method gave 0.98 and 0.99 per cent rubber. SO_4 was determined by the gravimetric method.

Sulfur dioxide is retained in the ash chiefly by whiting, which is converted into calcium sulfate. The solubility of the latter in water is 1:400. With the small contents of sulfur in most present-day rubber mixtures, 100 cc. of hot water will completely dissolve the calcium sulfate contained in the ash of an analytical sample.

Investigation of Resinite (Thiokol)

The new method was tested on American Thiokol and Soviet Resinite. The ignition of Thiokol in a tube proceeded smoothly, particularly in the presence of platinized asbestos. The determination was made with 5 or 6 pieces of rubber 0.05 to 1 g. in weight. Ignition was continued for about 3-4 minutes until the blue flame in the boat disappeared and only a gray trace remained. The entire sulfur passed into the receiver. Very small quantities of organic compounds and carbon dioxide were formed. The ash in the boat was determined. The solution in the receiver was boiled for 5 minutes to free it from hydrogen peroxide and carbon dioxide and titrated hot with 0.1 *N* NaOH in the presence of phenolphthalein.

The analytical results of Thiokol are shown in Table II (letters *a* and *b* indicate parallel determinations).

In the last column of the table are shown the values obtained by titration with barium chloride, in the presence of sodium rhodizonate, of the liquid evaporated after the titration in the presence of phenolphthalein.

Table II shows a mean of five determinations of Soviet Resinite by the gravimetric method of 80.43 per cent, and by titration in the presence of phenolphthalein in hot solutions 79.6 per cent sulfur.

TABLE II

No. Sample	Kind of Thiokol	Indicator	Sample	% Sulfur Volumetric Method	% Sulfur Gravimetric Method	% Sulfur Titrated with Na Rhodizonate
1a	American	Phenolphthalein, cold	0.0136	75.4
1b	American	Phenolphthalein, cold	0.0135	76
2a	American	Phenolphthalein, cold	0.014	81.7
2b	American	Phenolphthalein, cold	0.0138	77.2
3a	American	Methyl red	0.0212	73.7	83	..
3b	American	Methyl red	0.0202	74.3	84	..
4a	Soviet No. 3	Methyl red	0.0315	76.8	80.9	..
4b	Soviet No. 3	Methyl red	0.0278	74.5	80.6	..
5a	Soviet No. 3	Methyl red	0.035	78	78.51	..
5b	Soviet No. 3	Methyl red	0.0281	..	81.1	..
6a	Soviet No. 3	Methyl red	0.0427	78
7a	Soviet No. 3	Phenolphthalein, hot	0.0326	80	81.07	..
7b	Soviet No. 3	Phenolphthalein, hot	0.149	80
8a	Soviet No. 3	Phenolphthalein, hot	0.1365	80	...	79.9
9a	Soviet No. 3	Phenolphthalein, hot	0.102	78	...	27.8
9b	Soviet No. 3	Phenolphthalein, hot	0.1	80.4	...	80.2

The determination of sulfur in Resinite by the fusion method, in addition to the general shortcomings of this procedure, gave inconsistent values. The method recommended makes it possible to obtain in a short time sufficiently accurate results.

Litharge Rubber

The new method was tried in the determination of sulfur in rubber containing litharge. The preliminary ignition of lead sulfide by this method disclosed the presence of sulfuric acid in the receiver. A sample containing 2.9 per cent sulfur and 7 per cent litharge gave, as was expected, low values, *viz.*, from 1.48 to 1.76 per cent sulfur. The remaining sulfur was combined with lead.

Conclusions

1. The rapid method of determination of total sulfur and ash by ignition of rubber in a current of oxygen is not less accurate than the method of Henriques.
2. The proposed method can be used with all kinds of rubber mixtures except those containing litharge.
3. In the analysis of mixtures containing barytes, all sulfur except that contained in barytes is determined.
4. The method is particularly useful in the determination of sulfur and ash in Resinites (Thiokol), and the sulfate can be determined by the volumetric method.

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A Simplified Extrusion Plastometer for Unvulcanized Rubber

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Introduction

An extrusion plastometer operating at rates of shear comparable with those existing in rubber tubing machines has been described previously.¹ This plastometer was not designed to be a routine testing instrument, but rather was intended for use in the determination of the value of a high speed extrusion test for the factory control of rubber stocks. The plastometer served satisfactorily in the capacity of a research instrument, and has for some time been in constant use as a physical testing instrument where great rapidity of operation is not essential.

The results obtained with this plastometer were found to correlate with tubing machine behavior.² It was also found that the extrusion plastometer results agreed better with factory experience with various types of masticated rubber than did the Williams plastometer results.³ It was learned by experience with the extrusion plastometer, when used as a physical testing instrument, that its results agreed closely with calender behavior.

In many cases, it was found that the extrusion plastometer results did not correlate with the Williams plastometer results and that, in general, the extrusion plastometer appeared to be much more sensitive than the Williams plastometer.

The next step after establishing the value of the high speed extrusion test was to design an extrusion plastometer suitable for routine control testing. Such an instrument must be rugged in construction, rapid and simple in operation, and must yield precise results. The extrusion plastometer, which is described in this paper, was designed to fulfill these requirements and at the same time to give the same type of test results as those given by the original experimental plastometer.

Description of the Extrusion Plastometer

The new extrusion plastometer is illustrated in section in Fig. 1. The apparatus with which the extrusion is performed is shown at the right; the closing mechanism at the left. The two parts of the apparatus are linked together along line A-A.

The extrusion chamber consists of two members 3 and 4. The upper member 3 of the chamber has for its lower part a circular hardened steel knife edge 5 of diameter 7.62 cm. (3 in.) fitting into a circular groove in the lower member 4. The hardened steel extrusion die 2 is threaded into the lower member. The die is essentially the same as that employed with the original plastometer¹ and is 3.18 mm. ($\frac{1}{8}$ in.) in diameter and 4.77 mm. ($\frac{3}{16}$ in.) in length. Cartridge-type electric heating elements are mounted symmetrically in holes 6 in both top and bottom members of the chamber. The Bakelite members 15 provide thermal insulation for the chamber. The extrusion is performed by a steel piston 1.88 cm. ($\frac{3}{4}$ in.) in diameter which is actuated by a 17.8 cm. (7 in.) air piston. The stroke of the piston is limited to 1.88 cm. ($\frac{3}{4}$ in.) by a stop 27 and an adjustment screw 13. A turned ring 10 on the tail rod 9 actuates levers which make and break electrical contacts 11 and 12 at appropriate times just after the beginning and just before the

end of the stroke, respectively. Thus, at the beginning of the stroke, contact 12 is closed and contact 11 is open. Just after the beginning of the stroke, 11 is closed, completing the circuit with an elapsed time indicator which is accurate to within ± 0.05 second. The indicator runs until just before the end of the stroke when contact 12 is opened, breaking the circuit. The contact or housing members 17 are removable to permit adjustment of the contact by means of screws 16.

The temperature of the extrusion chamber is maintained constant to within $\pm 1^\circ \text{C}$. by means of a bimetallic spiral regulator mounted in a hole in the lower member 4 of the cavity. The contacts of the regulator actuate an inductive relay which makes and breaks part of the heating current through the cartridge heater coils. The temperatures of both upper and lower members 3 and 4 are measured by means of mercury-in-glass thermometers inserted in closely fitting holes.

The lower member of the chamber 4 is movable vertically through a distance of 7.6 cm. (3 in.) by means of the closing mechanism shown at the left of Fig. 1. The closing mechanism consists of a 17.8 cm. (7 in.) air cylinder 18 pivoted at 22,

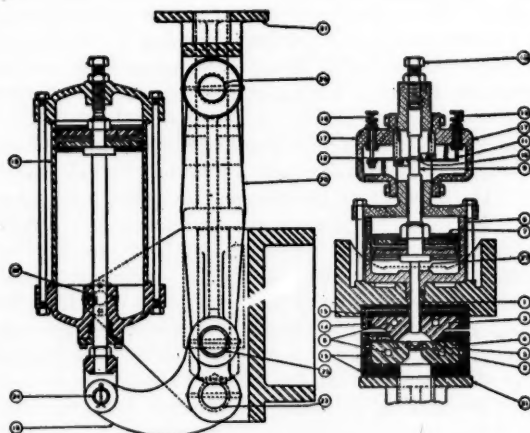


Figure 1—Simplified Extrusion Plastometer

a bell crank 19 and a toggle member 20. Downward motion of the air piston rotates the bell crank about pivot 23 and swings the lower end of the toggle to the left, thus lowering the lower member 4 of the chamber. Upward motion of the air piston closes the chamber. Because of the great mechanical advantage possessed by the air piston-toggle mechanism the lower element 4 can be pressed against the upward element 3 with a force of 45,000 kg. (50 tons) or more.

The plastometer is operated as follows. A slab of rubber stock taken from a mill and subsequently preheated to the testing temperature is folded once and placed on the lower member of the chamber 4. It is unnecessary to cut the slab to any particular size or shape except that it must be at least 1.88 cm. ($\frac{3}{4}$ in.) in thickness and 7.6 cm. (3 in.) square in the folded form. Air is admitted to the lower part of the air cylinder 18, thus activating the closing mechanism. As the member 4 is raised, the rubber is forced into the approximately hemispherical chamber, the excess extruding through the die 2. At the end of the closing operation, the chamber is completely filled with rubber. The air contained by the rubber either dissolves in the rubber or passes up past the extrusion piston 1 and out through the ducts 14. An interval of 15 to 40 seconds is required for the chamber

to close, depending on the type of rubber stock used. The rubber is allowed to remain in the chamber for a short period to compensate for inaccuracies in the temperature of the preheating device. The interval between placing the rubber on the lower member 4 and starting the extrusion piston 1 is 2.5 minutes with the present method of preheating (air ovens).

At the end of this interval, air is admitted to the top of the cylinder 8, thus driving the piston 1 downward and extruding a definite volume of rubber (5.45 cm.^3) through the die 2. The time required for the extrusion of this fixed volume is recorded by the elapsed time indicator and is taken as the plasticity index of the stock. The extrusion time varies from 2 to 60 seconds, depending on the type of stock being tested. An air pressure of 1.4 kg./cm.^2 (20 lbs./in.^2) is used with soft stocks and 2.1 kg./cm.^2 (30 lbs./in.^2) with tread stocks.

At the end of the extrusion, the chamber is opened. The rubber remaining in the chamber is removed and then the piston is raised. This last sequence of operations is quite important for, by removing the rubber from the chamber before raising the piston, sticking of rubber to piston and consequent clogging of the piston bearing are avoided. The rubber is removed from the upper part of the chamber by placing a piece of scrap rubber on the lower member 4, raising the lower member just to the point where the rubber in the upper member sticks to the piece of scrap rubber, again lowering 4 and removing the rubber from the upper member by pulling downward on the scrap rubber.

The method now employed for preheating the rubber samples consists in placing the samples in electrically heated ovens at 3-minute intervals and removing them at the same rate. The capacity of the ovens is such that 8 samples can be heated at one time, *i. e.*, each sample is preheated for 24 minutes. The temperatures of the ovens are maintained constant to within $\pm 0.5^\circ \text{ C.}$ by the use of bimetallic spiral regulators and efficient circulation of the air. Because of the variable thickness of the samples and the inefficiency inherent in the heat transfer from a gas to a poorly conducting solid, the temperatures of the samples are not as uniform as desired. Thus, as explained earlier, it is necessary to leave the samples 2.5 minutes in the plastometer chamber, so that the average total time of test is 3 minutes. With more efficient preheating, as would be furnished by a multiple platen press, the average time of test can be reduced to 1.5 minutes.⁵

Performance of the Extrusion Plastometer

The ruggedness of the simplified extrusion plastometer has been established by over two years of practically uninterrupted service. None of its parts have shown serious wear. In fact, the extrusion die, which was replaced after 2 years of service, was found to be enlarged only enough to cause a variation of less than ten per cent in the results as compared with those obtained with the new die.

No difficulty with friction in either the extrusion piston or the air piston has been experienced since the instrument was first lined up. To avoid frictional difficulties, the edges of the cup leathers were shaved very thin and they were thoroughly soaked in neat's-foot oil. Measurements are made thrice daily of the time required for the piston to complete its downward stroke with the air pressure in the cylinder reduced to 0.28 kg./cm.^2 (4 lbs./in.^2) and with no rubber in the chamber. This time is 0.1 second or less with the plastometer at the testing temperature 77.8° C. (172° F.). Possible starting friction is eliminated as a source of error by allowing the piston to travel a short distance (1 mm.) before starting the elapsed time recorder.

Error in the elapsed time indicator is less than ± 0.05 second. It is simply

a synchronous motor (1 r. p. s.) attached to a Veeder counter reading to 0.1 second. The fact that only one number is indicated by the device at the end of the extrusion practically eliminates human error of observation.

The matter of complete filling of the extrusion chamber has caused no trouble. In fact, rubber "biscuits" removed from the chamber either before or after extrusion are found to be entirely homogeneous. The fact that the chamber is filled completely is demonstrated by the uniformity of the extruded volume (see Table I).

The accuracy of the extrusion plastometer, with the samples preheated for 20 minutes in the extrusion chamber, is shown for three typical stocks in Table I. When the samples are preheated in the air ovens, the accuracy is somewhat less. However, even with inadequate preheating, the selectivity⁶ of the extrusion plastometer ranges from twice to twenty times that of the Williams plastometer when the two instruments correlate. When they fail to correlate, of course, the relative sensitivity of the two instruments has no meaning. The data of Table II give some indication of the manner in which the Williams plastometer and extrusion plastometer results compare on a regular factory skim stock.

TABLE I
ACCURACY OF EXTRUSION PLASTOMETER

Samples Preheated in Plastometer Chamber 20 Minutes at 77.8° C. (172° F.);
Driving Pressure—172 Kg./Cm.² (2460 Lbs./In.²).

Stock	Extrusion Time (Sec.)	Extruded Weight (G.)	Range (%)	Mean Deviation (%)
Inner tube	1.8	5.14	11	±2.8
	1.9	5.31		
	1.7	5.24		
	1.8	5.21		
Mill massed smoked sheet	23.1	4.61	19	±2.7
	23.7	4.60		
	25.7	4.62		
	27.8	4.57		
Tread	10.5	5.77	4.8	±1.4
	10.4	5.77		
	10.1	5.82		
	10.6	5.79		

TABLE II
SENSITIVITY OF EXTRUSION PLASTOMETER

TYPICAL "SKIM" MIXTURE

Batch	Williams Plastometer (Y ₂)	Extrusion Time (Sec.)
1	2.87	8.7
2	2.53	8.9
3	2.58	10
4	2.71	14
5	3.00	15
6	3.00	20
7	3.25	30
8	3.45	52
9	2.98	55

Conditions of Test

Extrusion plastometer: 20-minute preheat at 80° C. 20 lbs./in.² air pressure.

Williams plastometer: Y₂ is the separation of the plates after a 3-minute compression at 85° C.

Results

Data giving the relationships of the efflux rate *versus* driving pressure, temperature, etc., for the simplified extrusion plastometer, are omitted in this paper, since these relationships are the same as those found for the original experimental extrusion plastometer.¹ It is interesting to note, however, the difference between the plasticity-*versus*-temperature curves obtained with the original experimental extrusion plastometer and those obtained with the United States Rubber Company shearing disc plastometer.⁷ (See Fig. 2.) The data of Fig. 2 were obtained using the same batches of rubber in the two plastometers in each of the three cases, namely, unbroken (unmasticated) smoked sheet, mill-massed smoked sheet, and plasticized smoked sheet. For the case of unbroken rubber in the shearing disc plastometer, a negative temperature coefficient of plasticity was found in the higher temperature range in agreement with the results of Mooney.⁷ The other two curves for the shearing disc plastometer show very little change of plasticity

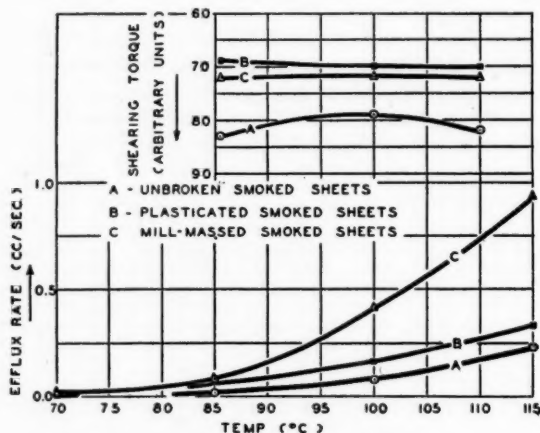


Figure 2—Plasticity Indices *vs.* Temperature

with temperature. On the other hand, the results of the extrusion plastometer show a rapid increase of the plasticity index with increasing temperature in all cases. Furthermore, the results of the shearing plastometer indicate that the plasticized rubber (1 pass through the Gordon plasticator) is softer than the mill-massed rubber, whereas the extrusion plastometer indicates just the opposite conclusion. These discrepancies between the results of the two instruments may be explained in part by the fact that the extrusion plastometer operates at a much higher rate of shear than the shearing plastometer. Another reason for this disagreement is that a certain amount of slippage takes place in the die of the extrusion plastometer, whereas slippage is excluded in the shearing plastometer. A third reason for the disagreement may lie in the fact that the observations of the shearing disc plastometer are made at thixotropic equilibrium, whereas those of the extrusion plastometer probably are not.

It should be noted that the two plastometers are designed on very different bases. The shearing disc plastometer is so constructed that a precise measurement of a fundamental physical property of rubber, the shearing viscosity, is obtained. The extrusion plastometer was built up with the idea of duplicating as

accurately as possible the conditions existing in processing machines and gives a more or less empirical measure of the softness of rubber stocks under these conditions. Without discussing further the relative desirabilities of these distinct types of testing instruments, suffice it to say that it has been found that the results of the simplified extrusion plastometer are entirely reliable in mill room control work. The ruggedness of the extrusion plastometer as well as its reasonably short testing cycle are qualities which make it a practical instrument for the routine testing of the plasticity of rubber stocks.

Acknowledgment

In conclusion, the author desires to express his appreciation to N. Johnston, R. W. Allen, and G. Watt for their parts in the development of the extrusion plastometer described in this paper and to N. A. Shepard, under whose direction this work was performed.

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- ¹ Dillon and Johnston, *Physics*, **4**, 225 (1933); *RUBBER CHEM. AND TECH.*, **7**, 248 (1934).
- ² Dillon and Torrance, *Ibid.*, **6**, 53 (1935).
- ³ Dillon, *Ind. Eng. Chem.*, **26**, 345 (1934); *RUBBER CHEM. AND TECH.*, **7**, 718 (1934).
- ⁴ The engineering design of the plastometer was made by R. W. Allen.
- ⁵ Since this article was prepared a method of preheating the rubber samples in a water-heated platen press has been developed and has been put into routine practice. With this method, the total time of test has been reduced to 1½ minutes and the accuracy of the test has been increased to a value equal to that given in Table I.
- ⁶ The "selectivity" is defined as the percentage difference between 2 observations on different mixtures divided by the average maximum percentage error.
- ⁷ Mooney, *Ind. Eng. Chem., Anal. Ed.*, **6**, 147 (1934); *RUBBER CHEM. AND TECH.*, **7**, 534 (1934).

An Improvement on the Williams Abrasion Tester

Tadao Ookita

SUMITOMO ELECTRICAL WIRE AND CABLE WORKS

There are many abrasion testing machines for rubber, each of which has its own merit or defect, and it is difficult to decide which is the best. Among these, the Williams abrasion machine is so constructed that the abrasion is expressible by the loss in volume per unit of work done on the rubber and gives relatively consistent values. But, since the results are not entirely satisfactory, various tests were carried out under various conditions with a new machine. A few improvements embodied in this model will be described here.

Figure 1 indicates the construction of the improved Williams abrasion tester. Two samples (A) of the required form are attached on the sample holder, which is located at the left end of beam C in the front part of the apparatus. Weight E is applied so that the sample is pressed on the abrasive surface B under a required pressure. The beam C is kept horizontal by applying weight D. A spring balance F on the right end is read at definite intervals of time during the test. The test is finished after 20 minutes, and the kilowatts are calculated from the weight D and the reading of the spring balance. The rate of abrasion is expressed by the loss in volume per kilowatt-hour.

Experimental

The rubber sample was prepared from 50 parts smoked sheet, 2 parts sulfur, 19.8 parts zinc oxide, 24 parts carbon, 4.2 parts softener and an accelerator, and vulcanized by steam at 30 lbs. per sq. in. pressure for 40 minutes.

Experiment 1. Effect of Preheating of the Vulcanization Mold and the Form of Mold

The mold, shown in Fig. 2-A, had a comparatively thick bottom and there was a danger of obtaining undervulcanized samples unless the mold was preheated. Therefore, a test was made to ascertain the effect of preheating on the rate of abrasion. Another test was made with a mold (Fig. 2-B) which had a thin bottom and therefore a low heat capacity. Vulcanization was therefore carried out without preheating.

TABLE I. RELATION BETWEEN THE METHOD OF VULCANIZATION AND THE RATE OF LOSS BY ABRASION

Method of Vulcanization	Rate of Abrasion Co. per Kilowatt-Hr.
Vulcanization with preheating mold A up to the temperature of vulcanization	302
Same as above except without preheating	293
Vulcanization without preheating mold B (thin)	279

During the test, the temperature was kept at 24-28° C. and the humidity at 65-70 per cent.

Preheating the mold thus had an effect on the results. It was necessary to preheat

when the type of mold shown in Fig. 2-A was used. Though the type of mold in Fig. 2-B did not require preheating, it was difficult to prepare good samples. The results were more satisfactory with the type shown in Fig. 2-A.

Experiment 2. Effect of Moisture during the Test

The details of the effects of temperature and of humidity on the abrasion testing of rubber are reported in *Ind. Eng. Chem., Analytical Ed.*, 1, 174 (1929), but the effect of humidity was not estimated since it changed with increase of temperature

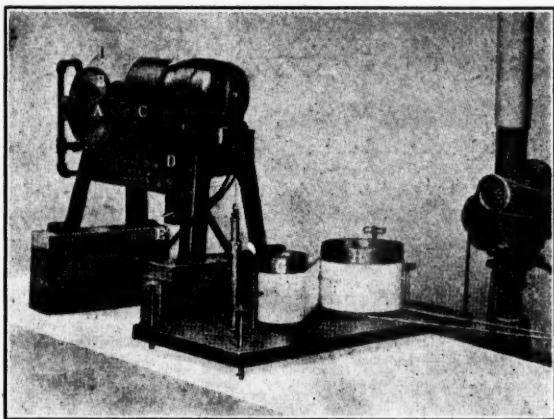


Figure 1—Improved Model of Williams Abrasion Tester

of the abrasion surface. There is only one other article, by Lambourn (*Trans. I.R.I.*, 4, 210 (1928)), in regard to this subject. Since it is thought to have considerable effect, a semi-quantitative test was made on the original Williams apparatus. Table II gives the averages of triplicate tests.

TABLE II. EFFECT OF HUMIDITY OF THE ROOM ON THE ABRASION OF RUBBER

Sample	Room Temp. °C.	Room Humidity %	Abrasion Cc. Per Kw.-Hr.
A	22-25	65-70	247
A	25	90-100	258
B	25	65-70	302
B	25	95-100	288

Samples A and B were the same except for different raw rubbers.

The rate of loss by abrasion was less with higher humidity, and there was about a 5 per cent difference in the rate of loss by abrasion with approximately 30 per cent difference in humidity. Accordingly, testing should be carried out under the same humidity in order to obtain uniform results. The compressed air used in the following experiment to sweep the wearing surface was dried by passing through a calcium chloride tower.

Experiment 3. Experimental Errors

No. 0 emery paper was used throughout as an abrasion surface, and the differences in the results with new paper for each test (Table III) were determined.

TABLE III. EXPERIMENTAL DEVIATIONS

Sample No.	Room Temp. °C.	Room Humidity %	Rate of Abrasion Co. per Kw.-Hr.
1	22	70	274
2	23	70	299
3	25	72	255
4	25	78	280
5	22	66	264
6	22	66	278
7	23	65	294
8	23	65	275
9	23	65	249
10	23	65	286
11	24	67	288
12	24	66	271
13	24	65	267
14	24	65	254
Average	23	68	274
Maximum	25	78	299
Minimum	22	65	249

There was thus found about ± 9 per cent deviation from the average value at the temperature $23^\circ \pm 3^\circ$ and humidity of $68 \pm 5\%$.

Experiment 4. Number of Times to Use Emery Paper

Williams states that the emery paper should be changed for each test, but Beaver (*Ind. Eng. Chem.*, 20, 895 (1928)) offers the opinion that it is unnecessary

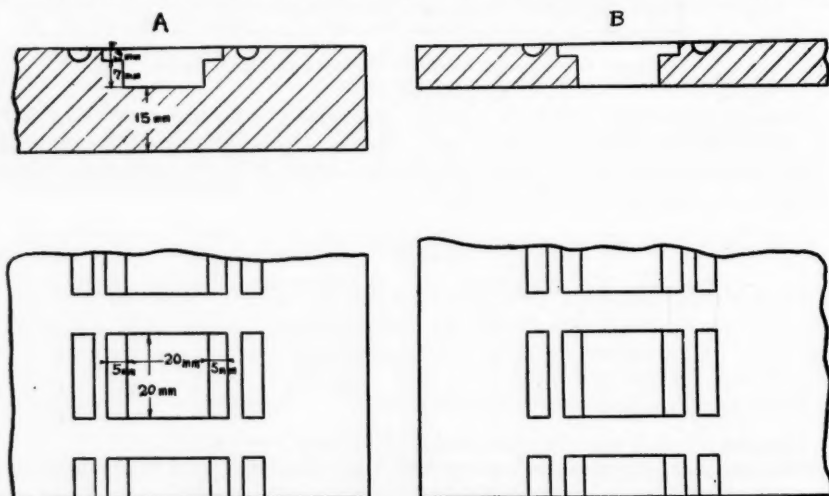


Figure 2—Molds for Vulcanization of Rubber for the Abrasion Test

to do this, though he does not mention the number of times to use the paper. Therefore a test was made to see how many tests could be made with one paper.

The temperature of the room was $22-23^\circ \text{C.}$, humidity 63–70 per cent.

The rate of abrasion in the 5th test was about 5 per cent lower than that in the first test. But the experimental deviations with each individual paper, as shown in Table III, reached ± 9 per cent when each test was made with a new paper; therefore, if 9 per cent deviation is allowable, it is possible to use a paper for nine

TABLE IV. DIFFERENCE IN THE RATE OF LOSS BY ABRASION BY REPEATED USE OF ONE EMERY PAPER

Emery Paper	Numbers of Use				
	1st	2nd	3rd	4th	5th
A	274	286	280	273	252
B	299	292	272	288	276
C	255	252	249	252	257
Average	276	277	267	271	262

tests. Since, however, an accurate result is not obtainable when the experimental deviation is great, it is better not to use emery paper for more than five tests.

Another point made by Williams is the effect of hysteresis of the abrasion surface on the rate of abrasion; taking this point of view into consideration, it is probably better to use new paper for each test.

Experiment 5. Substitute for Emery Paper

The emery paper to be used in this experiment (called standard emery hereafter) was inconvenient to purchase, and therefore a substitute was tested. At first, five No. 0 emery papers which had the same sized grains as those of standard emery paper were chosen. The test was made with new papers for each test; an average of four tests is given in Table V.

TABLE V. COMPARISON OF DIFFERENT EMERY PAPERS

Kind of Emery Paper	Made in	Temp. ° C.	Humidity %	Abrasion Co. per Kw.-Hr.	Vibration of Spring Balance
Sand	Japan	22-24	65-70	353	Much
Alloxide	Unknown	24-26	65-75	328	Less
National	Japan	24-26	65-75	368	Much
Emery	Abroad	25	70	319	Normal
Carborundum	Japan	26	70-75	398	Less
Standard emery	U. S. A.	22-25	65-75	274	Less

These emery papers were thin and had a tendency to bend toward the sample during the test; the rubber powder entered the space between the paper and supporting beam and the change in weight shown by the spring balance became irregular. In order to prevent this bending defect, a paper board was pasted on the back of the emery paper, and another test was made (Table VI).

TABLE VI. TEST WITH PAPER BOARD ON BACK OF EMERY PAPER

Kind of Emery Paper	Made in	Temp. ° C.	Humidity %	Abrasion Co. per Kw.-Hr.	Vibration of Spring Balance
Sand	Japan				Strong
Alloxide	Unknown	28	65	355	Less
National	Japan	29	65	376	Av.
Emery	Abroad	28	65-82	316	Av.
Carborundum	Japan	28	83	380	Less
Standard emery	U. S. A.	28	65	292	Less

The emery paper itself had the defect of bending, and this was not improved by pasting a paper board on the back of the paper. Accordingly, the above five papers were unsuitable.

Experiment 6. Improvement of Abrasion Machine and Measurements

The method of manipulation of this apparatus has already been described; the reading of the spring balance is difficult and inaccurate as the change is too great. To overcome this difficulty, the wattage required should be directly recorded, or the

reading of the spring balance should be automatically recorded, from which an average value could be obtained by using a planimeter. Since there was no convenient way of using the former method, the latter method was chosen.

Experiments 3 and 4 indicated that one piece of emery paper was not suitable for more than five tests, and an abrasive surface which would withstand many tests was therefore investigated. Carborundum whetstone made of Q quality carborundum of the same form as that of emery paper, but 1 cm. thick, was found to answer the purpose. The whole is shown in Fig. 1.

(A). *Improvement of the Spring Balance.*—The following improvements were made on the spring balance, including an automatic recorder. Beam C which holds the sample was made longer, and the spring balance was moved to the right of load D, so that the sample was at the center, was inverted and the lower end was attached to the base of the apparatus; at the top of the pointer, a pen point was attached to record the vertical motion of the pointer on the paper fixed on the cylinder of the automatic recorder. The cylinder could thus be rotated at two different speeds,

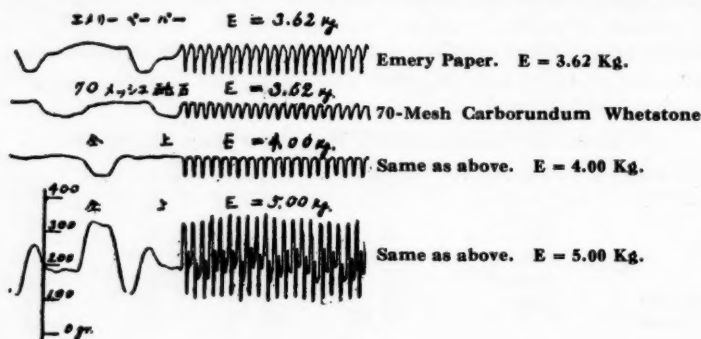


Figure 3

one by running with a clock device (9.3 cm. per second) and the other by rotation with an electric motor (116 cm. per second).

At first a record is made at low speed, then at high speed. After the test is over, the areas of curves corresponding to 5 revolutions over the abrasion surface at high speed are calculated with a planimeter and the average width is obtained by dividing by the length. The average weight is found from the table and the wattage is calculated from the average. The reason for running at two different speeds is that the calculation of the area is troublesome for low speeds and requires long recording paper at high speeds.

Since the construction of the beam which holds the sample is changed, the weight E to press the sample on the abrasive surface should be changed when necessary. For this reason, a test was made to find the relation between weight E, loss in volume and vibration of spring balance (Table VII and Fig. 3). In this test both a carborundum whetstone made of 70 mesh Q quality as well as a standard emery paper were used.

TABLE VII. THE RELATION BETWEEN WEIGHT E TO BE PRESSED AND THE RATE OF

Kind of Abrasion Surface	Time of Test Min.	ABRASION		Pressing Weight E Kg.	Degree of Abrasion Cc. Per Kw.-Hr
		Room Temp. °C.	Room Humidity %		
Carborundum whetstone	20	17-18	62-75	3.62	141
Carborundum whetstone	20	17	72-74	4.0	155
Carborundum whetstone	20	16-21	49-61	5.0	164
Emery paper	20	18-19	47-70	3.62	320

The pressing weight E used in this apparatus was usually 3.62 kilograms.

The least vibration was found when this weight of 3.62 kilograms was used. As 3.62 kilograms is an inconvenient unit, 4.0 kilograms was chosen, with a carborundum whetstone, and 20 minutes of abrasion.

(B). *Improvement of the Abrasion Surface.*—As stated already, the results with six kinds of sand papers were unsatisfactory. Carborundum whetstone can be used for many tests and was therefore chosen. The relation between the size of the grains of carborundum for the whetstone and the vibration of the spring balance was studied, since the least vibration is desirable. The pressing weight E was 4

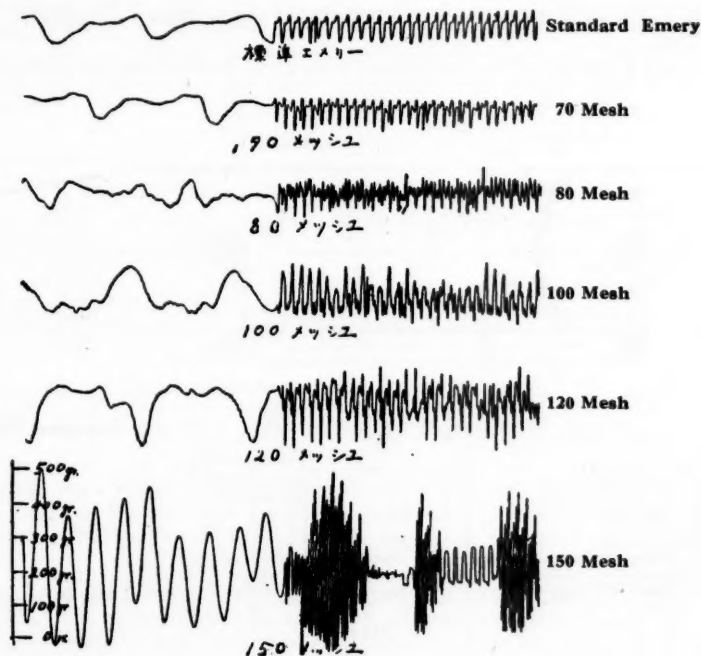


Figure 4

kilograms, and five carborundum whetstones made from 70, 80, 100, 120, and 150 mesh (No. 0) material, as well as a standard emery paper, were tested (Fig. 4).

A whetstone with 70-mesh carborundum gave the least vibration and was better than emery paper. Examination of the abraded surface of the rubber showed that 120 and 150 mesh gave less abrasion and became sticky, probably as a result of more heating. There was no great difference between 70 and 80 mesh carborundum. Although no measurement was made with less than 70 mesh, the results might have been better with larger grains if hysteresis had been taken into consideration.

(C). *Measurements with the Improved Apparatus.*—Improvements of the beam and spring balance have been described. Tests were made to determine the experimental errors in each with 70-mesh carborundum (which was the best) and a weight of 4 kilograms (Table VIII).

TABLE VIII. EXPERIMENTAL ERRORS WITH THE IMPROVED APPARATUS

Sample No.	Room Temp. ° C.	Room Humidity %	Rate of Abrasion Cc. per Kw.-Hr.
1	17	..	154
2	17	..	155
3	17	72	155
4	17	73	145
5	17	74	156
Average	17	73	155

The results were surprisingly good and much superior to those with emery paper. The rates of abrasion of twenty samples were calculated, and it was found that the errors in all the tests were within ± 5 per cent of the average value, except for one or two cases.

Tests were then made to see how many runs could be made on one piece of whet-

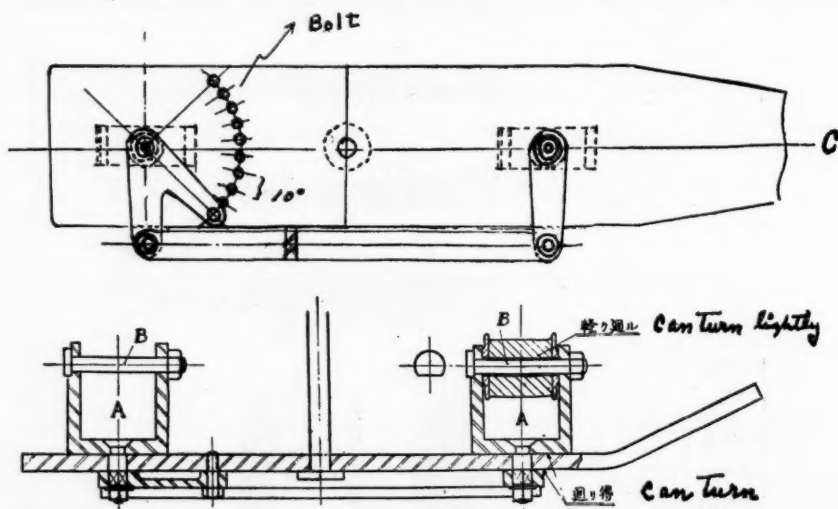


Figure 5

stone by using one side only, and also the effect of changing the surface on the rate of abrasion (Table IX).

TABLE IX. NUMBER OF TESTS OF CARBORUNDUM WHETSTONE

Surface No.	Time of Test Hr.	Room Temp. ° C.	Room Humidity %	Rate of Abrasion Cc. per Kw.-Hr.
1	up to 2	17	72-74	155
2	up to 2	17-20	59-65	132
1	over 50	18-19	60-63	153

The change in the rate of abrasion was very small even after 50 hours, and the errors were within 3 per cent, taking the effect of humidity of air into consideration. Therefore, if a 5 per cent error is allowed, the surface is usable for 100 hours or 300 tests.

Though no test was made on the effect of using different grades of carborundum whetstone, the preceding experiment showed approximately 13 per cent variations.

Accordingly, it was necessary to make abrasion tests with the same rubber sample to obtain a comparison of the rates of abrasion on different carborundum whetstones. For a series of tests on the rate of abrasion of rubber, it is best to use a carborundum whetstone, and for a comparison with other tests new emery paper for each test, taking the average of five tests.

Experiment 7. Measurements with Ring-Formed Samples

For making abrasion tests with this apparatus, it is necessary to vulcanize samples in round form in the mold indicated in Fig. 2 or the other method. But, since it is convenient to use this ring-formed sample in other apparatus, the angle machine designed by Vogt (*Ind. Eng. Chem.*, 20, 302 (1928)) was tested in the form indicated in Fig. 5. The part of beam C for supporting the sample is constructed,

TABLE X. COMPARATIVE TESTS WHEN THE DIFFERENT SAMPLES WERE AT THE RIGHT AND LEFT ENDS

Combination of Samples	Left End		Right End	
	Sample No.	Loss in Vol.	Sample No.	Loss in Vol.
1-1	1	0.048	1	0.046
2-2	2	1.837	2	1.618
3-3	3	1.670	3	1.652
1-2	1	0.024	2	1.015
2-3	2	1.637	3	1.665
3-1	3	1.173	1	-0.027**
2-1	2	1.081	1	0.014
3-2	3	1.800*	2	1.760
1-3	1	-0.016**	3	0.924

Remarks: * Abrasion loss very great.

** Increase in weight.

Density: No. 1, 1.306; No. 2, 1.530; No. 3, 1.782.

as shown in the graph in such a way that the cylindrical sample rotates with its center as an axis, while the angles of this axis and the center of beam C (C line) can be set at any desired angle from 3 to 63 degrees, with a capacity of 10 degrees shift each time.

The vibration of the spring balance was great even with regulation of weight E pressing on the abrasion surface, and with a change in the angle, and the volume loss per kilowatt-hour could not be estimated. Accordingly the rate of abrasion was determined only by estimating the loss in volume in a definite number of hours. When the length of sample was 2 cm. at an angle of 23 degrees, a pressing weight of 5 kilograms was found to give the least vibration of the spring balance. The abrasion was less when the angle was set at less than 23 degrees. When the angle was set at more than 50 degrees, there was a tendency for the sample to move outward from the rotation axis of the abrasion surface, making the estimation difficult. Accordingly, a suitable angle is 20 to 40 degrees. It was noticed that irregularity or difficulty of rotation of the sample had a great influence on the abrasion.

Experiment 8. Comparison of the Rate of Abrasion when the Right and the Left Ends of the Sample Are Different

For a comparison of more than two samples at a time, two samples are usually placed on the abrasion surface and their quality determined. The new apparatus can be used for such a purpose. In order to learn whether testing two samples at the same time influences the rate of abrasion of each sample, a qualitative test was

carried out. Sample No. 1 was compounded with 50 per cent carbon black, while No. 2 (Faber brand) and No. 3 (Lion brand) were eraser rubbers with high abrasion. These were made of the required size, and nine combinations were made by arranging them in the same way on both ends or differently on the right and left end. The results were averaged from three tests.

The abrasion tests were made using a 70-mesh carborundum whetstone with a pressing weight of 4 kilograms. The time was 3 minutes, as the abrasion of the eraser rubber sample was rapid. The results were not calculated as kilowatt-hours because it was difficult to figure the wattage; therefore, they were calculated as losses in volume in 3 minutes.

It is evident that there were great differences in the rates of abrasion by the method of combination of samples. The combination of more abrasive and less abrasive ones together showed in many cases less abrasion than did two like samples together. Such phenomena are possible with combinations of metals (cf. Patent Office Notice, June, 1933), and the theory will be published elsewhere by Saito.

For this reason, it is absolutely unsuitable to test two samples at one time with this or any other apparatus. Two different rubber samples at one time give irregular results as do two different metals at one time.

It seems that there is some influence of hysteresis, but no definite statement can be made here since no experiments have been carried out on this subject. In view of the results in Tables IV, IX, and others, the effect is probably not very great. However, where no compressed air is used, as with the other tester, the effect is great.

Summary

The Williams abrasion apparatus for rubber has various structural defects which are discussed. Certain improvements were therefore made.

1. It was proved experimentally that the effect of the humidity of the testing room is great, and that it is necessary to remove the abraded powder by a current of dry, compressed air.

2. It was found that emery paper can be used for five successive tests, but in this case there were 20 per cent variations, and 70-mesh carborundum whetstone was found necessary to reduce the errors. The maximum deviation with this whetstone was ± 5 per cent with twenty rubber samples. If this 5 per cent deviation is acceptable, carborundum can be used for 100 hours or 300 continuous tests.

3. The spring balance was constructed with an automatic recording device in order to obtain accurate weights. This improvement and the improvement of the abrasion surface increased the precision of the original Williams apparatus.

4. It is shown that large errors are encountered in testing more than two different samples at one time, as is the case in testing metals. This seems to be connected in some way with the hysteresis of the abrasive surface.

Thanks are due to Mr. Betsumiya, head of the Research Department for permission to publish this article and to Mr. T. Yamazaki and to Mr. S. Saito of the Sumitomo Steel Works for their kind advice.

Determination of Free Sulfur in Rubber Containing Mercaptobenzothiazole and Tetramethylthiuram Disulfide

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Free sulfur in a given vulcanizate is a definite and constant quantity. It can be extracted from rubber with acetone and various other sulfur solvents, and can be reduced directly in the rubber to hydrogen sulfide. The claim of Teny, supported by experimental evidence, that acetone extracts the entire sulfur in rubber has not been confirmed by other investigators.

Several methods for the determination of free sulfur in rubber are known. The classic method, adopted by the U. S. National Bureau of Standards, involves the extraction of sulfur with acetone and subsequent oxidation of the sulfur with bromine to sulfuric acid. The extraction consumes from 4 to 6 hours.

This method gives excellent results with rubber mixtures containing no sulfur-bearing accelerators. When sulfur-bearing accelerators are present in a rubber mixture, they are dissolved by acetone and may be oxidized together with the extracted sulfur by bromine.

To investigate the possible effect of accelerators (mercaptobenzothiazole and tetramethylthiuram disulfide) in a rubber mixture on the determination of free sulfur by the classic method, a series of experiments on the determination of sulfur in these accelerators under the conditions of analysis of free sulfur was undertaken.

Samples of each accelerator were oxidized with bromine as in the oxidation of free sulfur in acetone. After the oxidation tetramethylthiuram disulfide was completely dissolved, whereas mercaptobenzothiazole left a brown, insoluble resinous mass. Sulfur in the solutions was determined with barium chloride. These experiments gave varying results. A part of the sulfur (about one-half) in the accelerators is oxidized by bromine, and therefore the classic method of determination of free sulfur in rubber mixtures containing these accelerators gives somewhat high results, the degree of inaccuracy depending on the content of accelerator.

Another widely used procedure for the determination of free sulfur in rubber is the sulfite method of Bolotnikov and Gurova (*J. Rubber Ind.*, U. S. S. R., 10, 61 (1933); *RUBBER CHEM. AND TECH.*, 8, 87 (1935)).

The method depends on the extraction of free sulfur with sodium sulfite and the subsequent iodometric determination of the resulting thiosulfate. This method has considerable advantage over that of the Bureau of Standards because of its rapidity and the simplicity of operation. It was checked in various rubber laboratories, giving results equal to those obtained by the classic method. Unfortunately this method has the same shortcomings as the classic method, *i. e.*, it gives high values in analysis of rubbers compounded with accelerators containing sulfur. This disadvantage of the sulfite method is discussed by Taranenko (*J. Rubber Ind.*, U. S. S. R., 12, No. 4, 306-7 (1935)).

Sodium sulfite acts in this case as a solvent of accelerators and can be completely replaced by an alkali (Table I). The extracted accelerators are oxidized with iodine by the same method as with bromine.

TABLE I

Accelerator	Percentage Sulfur Determined by the Sulfite Method	
	Extraction with Na_2SO_3	Extraction with Alkali
Tetramethylthiuram disulfide	(1) 29.5; (2) 30.7	(1) 29.6; (2) 32.4
Mercaptobenzothiazole	18.4	18.5

Since the mechanism and the true coefficient of conversion of the oxidation of sulfur in the accelerators are not known, the determinations were calculated as in the analysis of rubber on the basis of 1 cc. of 0.1 N I corresponding to 0.0032 gram of sulfur. The results of separate experiments showed that in this case also a part of the sulfur is oxidized to sulfuric acid.

Hardman and Barbehenn (*Ind. Eng. Chem., Anal. Ed.*, 7, 103-4 (1935)) developed a method for the determination of free sulfur in the presence of polysulfidic (tetramethylthiuram disulfide) and sulfidic (mercaptobenzothiazole) sulfur. By this method a rubber sample is extracted for 6 to 8 hours with 50 cc. of acetone in the

TABLE II

Product	Percentage Free Sulfur		
	Hardman and Barbehenn Method	Sulfite Method	Bromine Method
Mixture No. 180	(1) 0.98; (2) 1.01; (3) 0.99	(1) 1.14; (2) 1.18	(1) 1.02; (2) 0.96
Thiuram mixture No. 2	(1) 0.04; (2) 0.02	(1) 0.37; (2) 0.37	(1) 0.85; (2) 0.85
Mercaptobenzothiazole	0.04	18.4	26
Tetramethylthiuram disulfide	0.11	(1) 29.5; (2) 30.7	22
Rubber Mixture No. 180			
Smoked sheet		100	
Sulfur		4	
Diphenylguanidine		0.5	
Zinc oxide		5	
Thiuram Mixture No. 2			
Smoked sheet		100	
Zinc oxide		5	
Tetramethylthiuram disulfide		3	
Stearic acid		1	

presence of a pure copper gauze spiral. After the acetone is poured out and the spiral is freed from the resinous matter by washing with fresh acetone, the flask with the dry spiral is closed with a rubber stopper fitted with a short and a long tube, the latter reaching nearly to the bottom of the flask. The short tube is connected by means of an interposed wash bottle with a receiver containing an ammoniacal solution of cadmium chloride (10 g. CdCl_2 , 200 cc. of water, and 300 cc. of concentrated NH_4OH). The cupric sulfide is decomposed with 20 cc. of concentrated hydrochloric acid, introduced into the flask through the short tube, by heating the assembly on a steam bath and allowing the liberated hydrogen sulfide to pass through the wash bottle into the receiver. After 5 minutes of heating, the assembly is removed from the steam bath and a current of air is passed through.

The following changes and additions in the Hardman and Barbehenn method are proposed as the result of a careful rechecking of the method.

1. To avoid any losses of cupric sulfide, the acetone extract is poured off through a filter.

2. The assembly is connected with the receiver through an interposing condenser as is usually done in the determination of hydrogen sulfide in sulfides.

3. Because the solution of cupric sulfide in hydrochloric acid proceeds with difficulty, the time required for driving off hydrogen sulfide is extended from 10 to 40-45 minutes.

4. The copper gauze is tested for any contaminating sulfur.

5. The absorption of hydrogen sulfide is best effected in a weak solution of acetic acid in the presence of sodium acetate for the neutralization of hydrochloric acid.

6. A current of carbon dioxide is passed through the assembly to prevent the oxidation of cadmium sulfide during the operation.

The modified method was checked in the analysis of tetramethylthiuram disulfide and mercaptobenzothiazole, in a rubber mixture containing neither of the two accelerators, and in a rubber mixture containing tetramethylthiuram disulfide and no sulfur.

The results of these experiments are shown in Table II.

It can be seen from the table that for the rubber mixtures without mercaptobenzothiazole and tetramethylthiuram disulfide this method gives results agreeing exactly with those obtained by the method of the Bureau of Standards.

Determinations of mercaptobenzothiazole and tetramethylthiuram disulfide alone by this method give traces of sulfur, which may be explained by contamination of the accelerators with elemental sulfur.

On the basis of these experiments it can be said that the method of Hardman and Barbehenn is the only accurate and convenient procedure for the determination of free sulfur in rubber mixtures containing tetramethylthiuram disulfide and mercaptobenzothiazole. Considering, however, that in ordinary rubber mixtures with their very small contents of accelerators, the errors caused by them seldom exceed 0.1 per cent, the use of the bromine and sulfite methods in routine factory analysis can be continued.

Determination of Free Sulfur in Rubber

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SINCE the determination of free sulfur in vulcanized rubber is an analytical operation of utmost importance, any improvement in technic which increases the accuracy and also shortens the time required is of considerable value. In practically all the methods used in the past, the sulfur has been extracted with hot acetone and then determined by various means: direct weighing (2), oxidation and estimation as barium sulfate, conversion into thiocyanate and titration with silver nitrate (3), reaction of copper gauze with sulfur and iodometric determination of the hydrogen sulfide evolved when the gauze is treated with acid (4), treatment with alcoholic potash and estimation of the sulfide and thiosulfate formed (5). These methods usually require 8 hours

TABLE I. CHECK DETERMINATIONS

Type of Stock	Free Sulfur	
	Gravimetric	Volumetric
	%	%
Tube	0.36	0.36
Tube	0.94	0.95
Tire tread	0.22	0.22
Mechanical	1.21	1.24
Uncured rubber-sulfur mix	32.20	32.40
	32.40	32.50
	32.40	32.60

or more for the extraction of the sulfur, and its estimation in the extract is a lengthy process.

Although much time is required for oxidation, precipitation, filtration, and weighing, the oxidation and gravimetric methods have proved best for routine work. Volumetric methods have not been satisfactory because of lack of satisfactory end points, side reactions, incomplete reactions, and tedious manipulations. The volumetric method to be discussed, however, makes it possible to shorten the time required for a free sulfur analysis to less than 3 hours per set of duplicate determinations.

In 1933 Bolotnikov and Gurova (1) introduced a volumetric method based on the fact that free sulfur is transformed into sodium thiosulfate when a rubber sample is heated in an aqueous solution of sodium sulfite. The authors have checked this method and have found the extraction and conversion into sodium thiosulfate to be complete and quan-

titative (as shown in Table I) in 2 hours when checked gravimetrically, using the Kratz, Flower, and Coolidge oxidation method on stocks containing non-sulfur-bearing accelerators.

When the method of extraction of the sulfur and its conversion into sodium thiosulfate were found to be quantitative, the authors set out to simplify the procedure and to make it a rapid and practical one for routine testing of rubber stocks containing sulfur-bearing as well as non-sulfur-bearing accelerators.

Improved Volumetric Method

The presence of mercaptobenzothiazole causes the thiosulfate method to give high results (due to oxidation of mercaptobenzothiazole to benzothiazyl disulfide) when compared with corrected results from the Kratz, Flower, and Coolidge method, obtained by subtracting the sulfur content of the mercaptobenzothiazole present from the results obtained by their gravimetric procedure. The mercaptobenzothiazole content was determined for this correction by extracting the rubber sample with acetone, treating the extract with a benzene solution of cupric oleate, and estimating the precipitated cuprous salt of mercaptobenzothiazole gravimetrically (6).

Since the correction cannot be conveniently made in the volumetric method, it was decided to separate mercaptobenzothiazole from the sodium sulfite solution by precipitation. Although the various metals noted below form precipitates which may be filtered out, only the cadmium salt was found to be satisfactory in this case. Silver reacts with the thiosulfate to form silver sulfide. Lead thiosulfate is only sparingly soluble. Cuprous copper will react quantitatively with mercaptobenzothiazole, but any cupric copper will oxidize thiosulfate. Cadmium alone of all the metals tried precipitated mercaptobenzothiazole without reaction with thiosulfate.

The addition of 5 mg. of sodium stearate (which serves as a wetting agent in the extraction) and 0.5 gram of paraffin (which prevents frothing) were found to be beneficial. Air condensers are unnecessary, since cover glasses work satisfactorily when paraffin is used.

The fatty acids present in rubber stocks are extracted during the heating with sodium sulfite. These are precipitated along with the fatty acid from the soap by a solution of strontium chloride. The excess strontium forms insoluble strontium sulfite which helps to break up the other flocculent precipitates, thus keeping the filters from clogging.

Since the final titration is a thiosulfate-iodine reaction, it is necessary to eliminate or render inert the excess sodium sulfite. The addition of formaldehyde accomplishes this by forming a formaldehyde-sodium sulfite addition product.

The end point is improved by using a large volume (approximately 600 cc.) of solution acidified with acetic acid,

and cooled below 15° C. with crushed ice. A very distinct end point is obtained which will last 2 to 3 minutes.

Procedure

Place 2 grams of thinly sheeted sample 0.05 to 0.075 cm. (0.02 to 0.03 inch) in a 400-cc. Underwriters' flask. Add 100 cc. of 5 per cent sodium sulfite solution, 5 cc. of a 0.1 per cent sodium stearate suspension in water, and approximately 1 gram of paraffin. Cover the flask with a small watch glass and heat so as to boil gently for 2 hours. Remove the flask and add 100 cc. of 0.5 per cent strontium chloride solution and 10 cc. of 3 per cent cadmium acetate solution. Separate the rubber and precipitates

TABLE II. COMPARATIVE DETERMINATIONS

(Stocks containing non-sulfur-bearing accelerators)

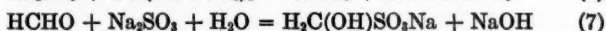
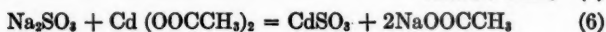
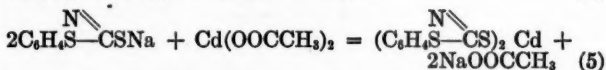
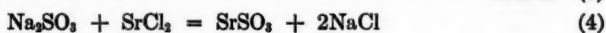
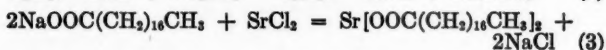
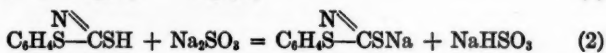
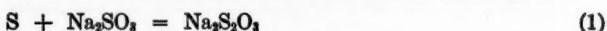
Sample	Free Sulfur	
	Gravimetric %	Thiosulfate %
Tread	0.53	0.49
	0.49	0.44
	0.21	0.19
	0.36	0.35
	0.22	0.23
	0.07	0.07
	1.05	1.02
Cushion	1.00	0.99
	0.79	0.75
	0.75	0.71
Carcass	0.53	0.50
	0.25	0.22
	0.37	0.36
	0.20	0.18
Tube	1.00	0.98
	0.52	0.52
	1.02	0.98
	0.52	0.52
Valve bases	0.15	0.13
	0.52	0.51
	0.87	0.84
	0.88	0.87
	0.18	0.16
	0.04	0.05

TABLE III. COMPARATIVE DETERMINATIONS

(Stocks containing mercaptobenzothiazole)

Sample	Free Sulfur	
	Corrected gravimetric %	Thiosulfate %
Tread	0.15	0.16
	0.46	0.47
	0.11	0.15
	0.23	0.21
	0.54	0.52
	0.43	0.43
Carcass	0.20	0.22
	0.42	0.39
	0.82	0.78
	0.25	0.29
	0.26	0.24
Tube	0.36	0.36
	0.23	0.19
	0.11	0.07
	0.05	0.04
	0.01	0.01
	0.07	0.08
Juvenile tires	0.75	0.78
	0.43	0.46

by filtration, using a Büchner funnel with suction. Wash with two 75- to 100-cc. portions of a wash solution containing 40 cc. of 3 per cent cadmium acetate solution per liter. (The funnels are prepared by forming a thin asbestos pad over a single sheet of qualitative filter paper. Filters thus prepared can be used numerous times.) To the filtrate, add with stirring 5 cc. of 40 per cent formalin solution, 10 cc. of glacial acetic acid, and 5 cc. of 1 per cent starch solution. Add enough crushed ice to bring the temperature of the solution below 15° C., and titrate with a standard solution of iodine to a blue end point. A blank determination is run on the reagents and this figure, usually 0.2 to 0.3 cc., is subtracted from the titrations on the samples.



From Equations 1 and 8 it is evident that one equivalent of iodine is required for each equivalent of sulfur; hence 1 cc. of a 0.1 *N* solution would be equal to 0.003206 gram of sulfur. It has been found convenient to use 0.0624 *N* iodine solution, so that 1 cc. is equivalent to 0.00200 gram of sulfur or 0.10 per cent free sulfur on a 2-gram sample.

Discussion of Results

A comparison of results obtained by both the Kratz, Flower, and Coolidge and the thiosulfate methods (Table II), on stocks containing non-sulfur-bearing accelerators, shows that the volumetric method usually gives results very slightly lower than the gravimetric, the maximum being 0.05 per cent on the compound.

A similar comparison (Table III) was made on stocks containing mercaptobenzothiazole as a representative sulfur-bearing accelerator of wide usage. The amount of sulfur in the acetone extract which was determined to be organically combined as mercaptobenzothiazole was subtracted from the gravimetric value to give the corrected gravimetric free sulfur value.

The comparative figures show an agreement between the two methods which is extremely good and within the experimental errors involved, and are offered as proof that the thiosulfate method obtains free sulfur values that are of practical worth in a minimum of time.

In addition to all common fillers, softeners, etc., the following compounds have no effect upon the accuracy of the method:

TABLE IV. DETERMINATIONS ON MERCAPTOBENZOTHAZOLE TREAD STOCKS

Gravimetric Free Sulfur %	Correction %	Gravimetric Free Sulfur Corrected %	Thiosulfate %
0.67	0.09	0.58	0.61
0.38	0.14	0.24	0.24
0.36	0.02	0.34	0.35
0.72	0.27	0.45	0.43
0.78	0.27	0.51	0.51
0.85	0.28	0.57	0.57
0.54	0.16	0.38	0.40

TABLE V. COMPARISON OF METHODS

Stock	Free Sulfur			
	Katz, Flower and Coolidge Corrected		Bromine	Thio- sulfate
	%	%	%	%
Guanidine	0.35	0.34	0.34
	0.72	0.70	0.69
	0.71	0.72	0.71
	0.79	0.74	0.74
Mercaptobenzothiazole	0.85	0.57	0.68	0.57
	0.72	0.45	0.56	0.43
	0.50	0.37	0.36	0.34
	0.26	0.10	0.18	0.13
	0.48	0.32	0.39	0.35

thiocarbanilide, guanidines, aldehyde amines, tetramethylthiuram monosulfide, mercaptobenzothiazole, benzothiazyl disulfide, *p*-aminophenol, naphthylamines, xanthates, carbamates, and vulcone.

Accelerators such as tetramethylthiuram disulfide, which also function as vulcanizing agents, liberate the available sulfur during the heating with sodium sulfite and the thiosulfate thus formed influences the accuracy of the free sulfur determination on such stock. This is perhaps no serious handicap because gravimetric results on such stocks are of no particular value because of the high percentage of organically combined sulfur in the acetone extract.

Conclusions

Values obtained by the volumetric method herein described compare favorably with those obtained by gravimetric methods when corrections are applied to the latter for the sulfur in the organic compounds in the acetone extract.

The precision of the method is excellent, as duplicates in each set usually check within 0.01 per cent of free sulfur on the compound.

This method is much faster than previous methods.

The cost of the reagents is low when compared with most other methods.

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An Impact Cutting Test for Tire Tread Stocks

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THE importance of the problem of pneumatic tire tread cracking is generally recognized by rubber technologists. The closely allied problem of tread cutting, however, has received comparatively little attention in the literature (2-5, 7). This fact is surprising in view of the possible causal nature of cutting with respect to cracking. The published work on cutting of rubber stocks, referred to above, all deals with what may be termed static tests—that is, the cutting tools employed were applied to the rubber test pieces with velocities much lower than those with which a tread button impinges on an obstacle in normal service. Some of these tests (3, 4, 5) were designed for evaluating cutting resistance of rubber-insulated electric conductors. The methods described in these papers are satisfactory for evaluating the cutting resistance of rubber insulating materials, but fail in some cases to evaluate correctly the cutting resistance of tire tread stocks. In the most recent of these papers, which deals specifically with the cutting of tire treads, Clarke (1) using a slow-moving cutting tool (15 cm., 6 inches, per minute) drew conclusions concerning the relative values of various compounding ingredients in increasing or decreasing cutting resistance. None of Clarke's conclusions was radically different from those found in the impact tests described in this paper. (The unpublished preliminary work on impact cutting tests at this laboratory, carried out by J. H. Howey and B. A. Jones with a small pendulum device, led to the considerations underlying the test to be described.)

Theoretical Aspects of Tread Cutting

It should be borne in mind that the cutting resistance of a rubber stock is a very complex function of several interrelated factors, some of which are themselves complex. The most important of these factors are hardness, tear resistance, elastic modulus, tensile strength, aging resistance, and temperature. At first thought, it might seem desirable to determine the functional relationship between cutting resistance and these factors and thus evaluate cutting resistance in terms of simpler quantities. This procedure has not proved practicable in the experiments performed in this laboratory, for it was not found possible to express this relationship as a simple, single-valued function. For example, it was found that, in general,

cutting resistance increased with increasing hardness but, in certain cases, a stock with a greater hardness than another stock was worse from the standpoint of cutting. Hence, it was concluded that cutting resistance should be evaluated by a special cutting test.

A distinction should be made between initiation of a cut in a tire tread and the consequent growth of the cut into a cracking or chipping failure. The initiation of the cut depends on that property which will hereafter be referred to as "cutting resistance." The growth of the cut depends greatly on tear resistance, which itself is a function of frequency of flexing, resistance to oxidation, and many other factors.

In developing an empirical test, which a cutting test must be, it is desirable to incorporate in it as accurately as possible the factors existing in service. In the case of the cutting test it was possible to use the same order of impact velocities and forces with which a tread button impinges on a sharp obstacle in the road. The exact form of the cutting object could not be reproduced. Thus, it was necessary to use an arbitrarily designed wedge. A 20° steel wedge was selected mainly because it gave reproducible cuts of reasonable depths using the velocities and impact forces with which a tread button strikes an obstacle.

The impact velocity of a tread button on an obstacle of height y was calculated on the assumption that the tire is a rigid hoop of outer diameter $2a$ rolling on a horizontal plane with angular velocity ω . The expression for the impact velocity V thus deduced from the equations of a cycloid is:

$$V = \omega\sqrt{y} \sqrt{2a - y} \quad (1)$$

This expression is only approximate for a deformable pneumatic tire for, sidewise bulging neglected, only the extreme shoulder portions of the tread have pure cycloidal motion. However, Equation 1 gives at least the order of magnitude of the impact velocity in the central portion of the tread.

The impact force S was calculated as follows: Consider a body of weight P striking a relatively immovable body with velocity V and causing an instantaneous deformation d . The energy stored in the immovable body is $Sd/2$ and is equal to the sum of the kinetic energy of the moving body at impact ($PV^2/2g$) and the work, Pd , done by the movable body in traversing the distance d . Hence,

$$\frac{Sd}{2} = \frac{PV^2}{2g} + Pd \quad (2)$$

If e is the static deformation for a load P , by Hooke's law

$$\frac{S}{P} = \frac{d}{e} \quad (3)$$

Eliminating d from Equations 2 and 3 gives

$$eS^2 - 2ePS - \frac{P^2V^2}{g} = 0 \quad (4)$$

The solution of Equation 4 is

$$S = P + P \sqrt{1 + \frac{V^2}{eg}} \quad (5)$$

which relates the momentary maximum force or impact force S and the static load P . (This equation is not original with the author but is derived here for the convenience of the reader. For a similar expression see 6.)

Equation 5 can be applied directly to the case of a cutting obstacle impinging on a tire with velocity V given by Equation 1. Thus by Equations 1 and 5,

$$S = P + P \sqrt{1 + \frac{\omega^2 y}{eg} (2a - y)} \quad (6)$$

or, for small values of y ($0 < y < 2.5$ cm.) where $e \cong y$,

$$S = P + P \sqrt{1 + \frac{2a\omega^2}{g}} \quad (7)$$

In Equation 7, ω and a are known. The factor P is simply a function of y or the static load applied to a cutting edge to cause a deflection y without actually cutting the rubber.

In order to determine P for various static deflections e , a device was employed by means of which a 20° steel wedge was pressed against the contact area of the tread of a normally inflated and loaded tire. In this manner, a load-deflection curve was determined from which the values of P corresponding to various values of $e = y$ were directly obtained. Inserting these values of P into Equation 4, the impact force S was calculated. Values of impact velocity and impact force, calculated from Equations 1 and 7, respectively, are given in Table I.

TABLE I. IMPACT VELOCITY AND IMPACT FORCE

(Heavy-duty tire 81×15.2 cm.; rolling radius, 38.9 cm.)

Car Speed	Obstacle Height 0.25 Cm.		Obstacle Height 0.62 Cm.		Obstacle Height 2.5 Cm.	
	Velocity	Force	Velocity	Force	Velocity	Force
Km./hr.	Cm./sec.	Kg./cm.	Cm./sec.	Kg./cm.	Cm./sec.	Kg./cm.
16.1	52	62	79	163	158	775
32.2	104	124	158	326	316	1550
64.4	208	248	316	652	632	3100
96.6	312	372	474	978	948	4650

The simplest type of apparatus which could be used with these values of impact velocity and force appeared to be a steel knife falling freely under gravity. For such a device, the impact velocity would be determined by the height of free fall and the impact force by the load attached to the falling knife. The relation between the load, L , on the knife and the impact force is obtained directly from Equation 2 by replacing $\frac{V^2}{2g}$ by h and takes the form

$$S = 2L \left(1 + \frac{h}{d} \right) \quad (8)$$

where h is the height of fall and d is the depth of penetration of the knife before cutting occurs.

In the impact cutting device, described in detail below, the impact velocities ranged from 300 to 600 cm. per second, and the impact forces varied from 360 to 1200 kg. per cm. of knife edge. Comparing these actual values of velocity and force used on the apparatus with the calculated values of Table I, it is seen that the impact cutting device could be operated under conditions approximating those found in road service.

It is true that the tread rubber on a tire is mounted on a pneumatic base, whereas the test piece of the impact cutting test was a rubber block, 12.7 cm. (5 inches) in length, 1.9 cm. (0.75 inch) in width, and 3.8 cm. (1.5 inches) in height, mounted on a heavy steel platen. However, it was thought that the use of a pneumatic backing for the test block of the impact cutting device would introduce into the test a variable very difficult to control. Thus, the pneumatic backing of a tire was simulated qualitatively by using a rather tall (3.8 cm.), and therefore highly deformable, test block.

Apparatus and Analysis of Results

The impact cutting device illustrated in Figure 1 consists, mainly, of an accurate vertical slide which guides a loaded knife in approximately free fall. The slide is rigidly suspended from the top end. The knife, which is a 20° wedge of altitude 3.8 cm. (1.5 inches) and has an edge of 7.6 cm. (3 inches), impinges on a rubber test block and produces a cut which can be measured with an ordinary steel scale. The sliding Dowmetal carriage which bears the knife is constructed so as to permit different combinations of weights to be attached to it. The knife is readily detachable and is removed from the machine after each series of tests, oiled, and kept in a closed box until needed again.

The machine is also equipped with a vertically movable electromagnet with which the knife and carriage can be raised to the desired height and released by reversing the current in the coils of the magnet. The magnet is raised and lowered by means of a windlass. The slide is equipped with a number of stops (not shown in Figure 1) set at known heights, which can be used by the operator to ascertain when the carriage has been raised to the correct height. Two rubber bumpers at the bottom of the slide cushion the blow of the carriage and make it impossible for the knife edge to hit the platen face. Blocks of certain stocks deform to such an extent that the carriage hits the bumpers before completion of the cut. A trip device (not shown) mounted at the base of the slide, lights a small lamp when the carriage strikes the bumpers. In cases where the light is thus turned on, the test results are discarded.

The rubber test block, $12.7 \times 1.9 \times 3.8$ cm. ($5 \times 0.75 \times 1.5$ inches), is placed in a holder at the bottom of the slide and rests on the large face of a steel platen $51 \times 51 \times 10$ cm. ($20 \times 20 \times 4$ inches). The block rests on its 12.7×1.9 cm. (5×0.75 inch) face with its long axis perpendicular to the knife edge. Two cuts are made in each block at positions 3.2 cm. (1.25 inches) from the ends of the block. The deeper cuts are usually uniform in depth across the width of the block and can thus be measured with a steel scale after slitting through the rubber remaining at the bottom of the cut. The shallow cuts are, in general, less regular in depth than the deep cuts. However, with

a little practice, the operator can estimate the average depth of the shallow cuts without much difficulty.

The cutting knife is of hardened steel and is carefully ground in the form of a 20° wedge. The feather edge is removed from the knife with a fine abrasive cloth. The sharpness of the knife changed with use but, by always running a control stock simultaneously with an experimental stock, it was found that the relative cutting results were essentially uniform over a period of 2 years. In this study of the aging of the knife edge, the effect of the aging of the rubber was avoided by using new samples.

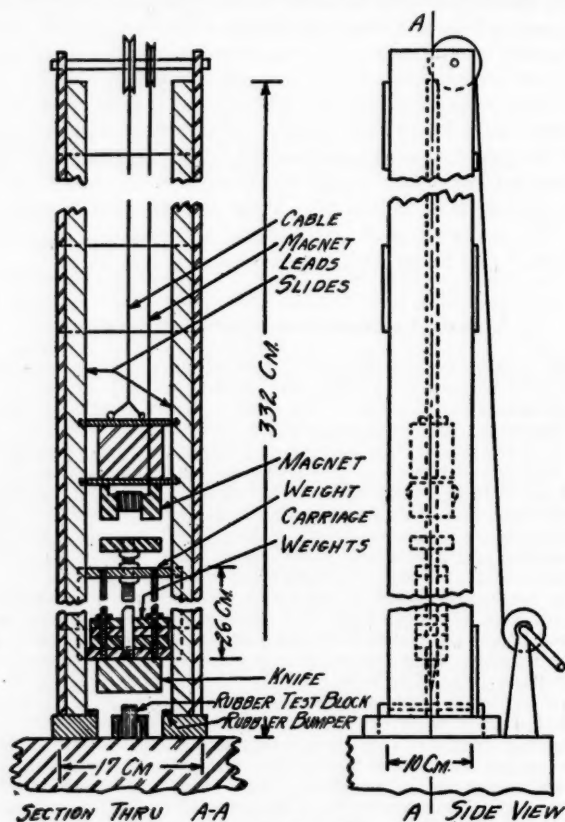


FIGURE 1. IMPACT CUTTING APPARATUS

In the method of testing adopted as standard, at least six test blocks of each stock or cure to be tested are cured in a 12-cavity mold in a press, the temperature of which is very carefully controlled. The blocks are then set aside for 1 week to allow the cutting resistance to come to a stable state. The hardness is then measured with a Firestone 1.36-kg. (3-pound) penetrometer (8) at various points on the 12.7×1.9 cm. face of the blocks. Two cuts are then made in each block with the impact cutting machine, as described above. Thus, using six blocks, it is possible to obtain twelve cuts in each stock or cure. These cuts are usually made at 2 or more loads chosen to give a depth of cut vs. load (D vs. L) curve. The cutting velocity is usually

set at 424 cm. per second (13.9 feet per second). In practically every case the D vs. L curve is linear (Figure 2).

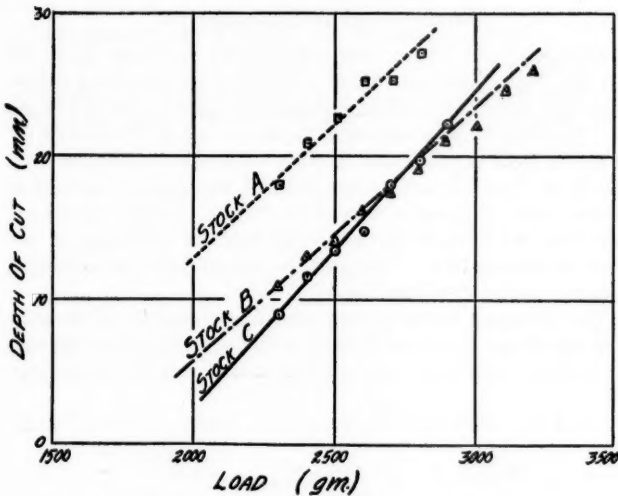


FIGURE 2. DEPTH OF CUT vs. IMPACT LOAD
20° knife, velocity 488 cm. per second

To be very exact, there are two physically independent indexes of cutting resistance—i. e., the slope of the D vs. L curve and the extrapolated load intercept. However, it is difficult to interpret data on the basis of two indexes. Hence,

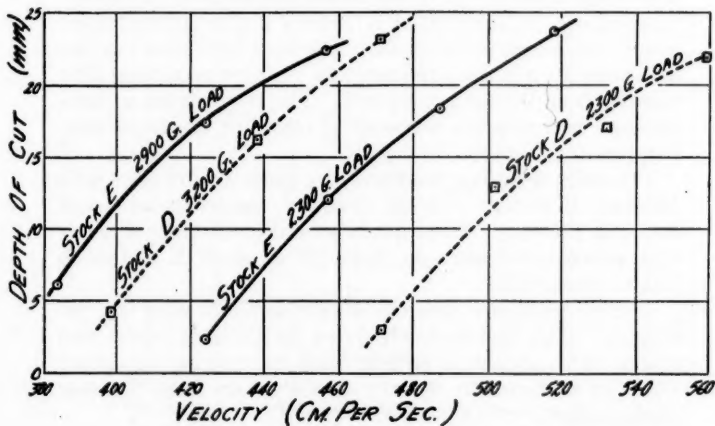


FIGURE 3. DEPTH OF CUT vs. IMPACT VELOCITY
20° knife

the load necessary to give a 25-mm. cut, L_{25} , has been selected as a single cutting index. This index, L_{25} , has been found very satisfactory, in that results arrived at through its use

agree with road test results and with results evaluated by means of the slopes and load intercepts of the D vs. L curves.

Functional Relationships

As mentioned above, the relationship between depth of cut and load is linear. That both the slope and load intercept vary for different stocks is clearly demonstrated in Figure 2. The relationship between depth of cut and velocity at constant load is not linear, however (Figure 3). In general, the D vs. V curves are convex upward, though occasionally a curve which is concave upward is found. Unlike the D vs. L curves, the D vs. V curves do not cross in the range of velocities investigated. The practice of running tests at a single velocity is therefore justified.

The curves of Figure 4 show that L_{25} , a measure of the cutting resistance, decreases rapidly with increasing temperature. In making these tests, the test blocks were kept in an ice box

TABLE II. CUTTING RESISTANCE vs. RESISTANCE TO TEAR

Stock	L_m Grams	Hand Tear Estimate
A	4300	Best
B	4040	Very good
C	4180	Very good
D	4230	Very good
E	4350	Good
F	4390	Fair
G	4360	Fair

or oven until the center of the blocks had reached the desired temperature, as measured by a mercury-in-glass thermometer inserted in a hole in the block. The tests were then run immediately to minimize temperature changes occurring after removal from the oven or ice box. This dependence on temperature indicates the necessity of recording the room temperature for all tests.

The index of cutting resistance, L_{25} , generally increases with hardness (Firestone 1.36-kg. (3-pound) penetrometer) as is shown in Figure 5. However, in several cases, distinct reversals occurred—for example, stock IX vs. stock X and stock VII vs. stock VIII.

Cutting resistance does not always correlate with tear resistance. This fact is clearly shown in Table II, where two stocks which appear to be best from the cutting standpoint show up as distinctly inferior to the others from the tear standpoint.

The accuracy of the results of the impact cutting test depends upon the number of tests averaged. For example, where six blocks of a given stock were tested, the mean deviation was 4 per cent; where twelve blocks were tested, the mean deviation was 3 per cent. In individual cases the accuracy is much greater and can be determined in

each case—for example, the mean deviations for the tests of Table IV were much less than 3 per cent.

Compounding Trends in Resistance to Cutting

The cutting resistance generally increased with the carbon black loading, as is shown in Figure 6. To obtain these

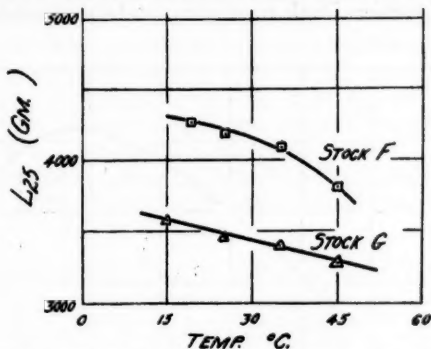


FIGURE 4. CUTTING RESISTANCE vs. TEMPERATURE

20° knife, velocity 424 cm. per second

data, the carbon black content in a commercial mercapto-benzothiazole tread stock was varied so as to give loadings varying from 38 to 76 parts by weight per 100 parts of rubber. It may be seen that the cutting resistance increased with in-

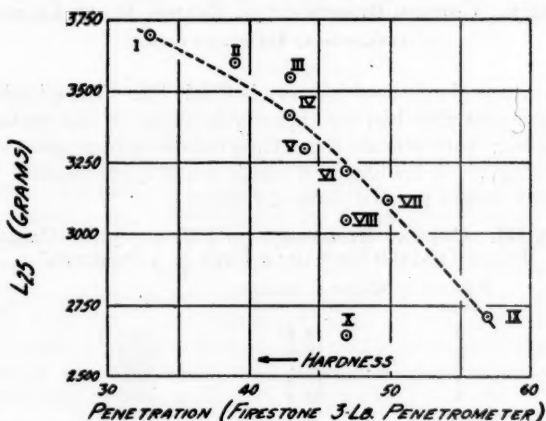


FIGURE 5. CUTTING RESISTANCE vs. HARDNESS

Ten stocks; each point average of 12 tests; 20° knife; velocity 424 cm. per second

creasing carbon black loading up to a loading of 67 per cent and then began to decrease. The existence of this maximum in cutting resistance with respect to carbon black loading has

very little practical significance, since 67 per cent black is considerably above present practical compounding limits for treads. However, the fact that the cutting resistance increases to that point indicates that, for special types of service where cutting resistance is the major consideration, the loading of carbon black should be increased above the limits considered satisfactory for other types of service.

The effect upon the cutting resistance of varying the amount of carbon black in a mercaptobenzothiazole tread

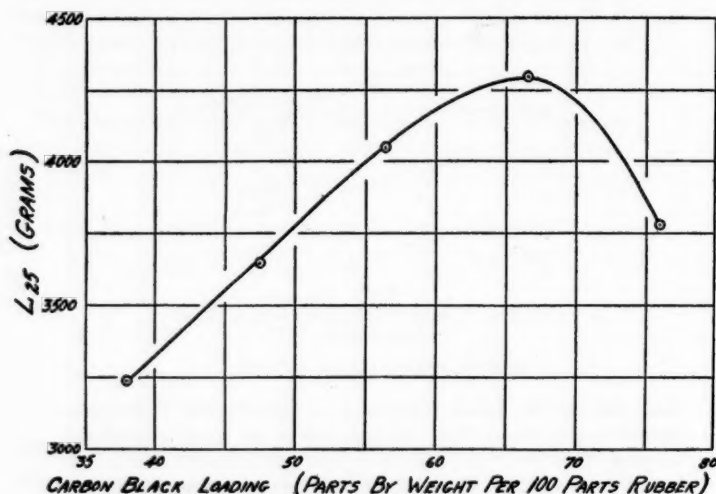


FIGURE 6. CUTTING RESISTANCE vs. CARBON BLACK LOADING
20° knife, velocity 424 cm. per second

stock where glue is used is shown in Table III. The addition of 5 per cent glue had no appreciable effect on the cutting resistance; furthermore, the cutting resistance increased with increasing black loading to a maximum at approximately 57 parts by weight per 100 parts of rubber.

TABLE III. CUTTING RESISTANCE AS A FUNCTION OF CARBON BLACK LOADING WITH GLUE USED AS A SOFTENER

Per cent by Weight on Rubber Glue	Carbon black	L ₂₅
0	49.4	4600
5	49.4	4650
5	53.7	4760
5	57.0	5000
5	60.0	4990

Comparison of Impact Cutting with Road Tests

Great care must be exercised in comparing the results of a laboratory cutting test with road test results, for most so-called cutting tests on the road involve cracking as well as

cutting. In fact, it was found necessary to devise a special road cutting test. In this test, half-and-half tires mounted on a truck were run at low speeds over a specially constructed road upon which were strewn sharp pieces of furnace slag, broken insulators, etc. The tires were removed from the rims, after 200 to 500 miles of this service, in a badly cut and chipped condition. The treads were then cut up in such a manner that the areas of all the individual cuts could be measured. The amount of cutting sustained by a stock in the test was assumed to be proportional to the total area of the cuts. Six stock comparisons were made in this manner. Cutting test blocks were cured from sections of the extruded treads which were actually used in the test tires and impact tests were made in the standard manner.

The results are given in Table IV. The results of the impact cutting test correlated with the road test results in all cases.

TABLE IV. IMPACT TESTS *vs.* ROAD TESTS

Tire	Stock	Road Test Evaluation	(81 × 15.2 cm. tires)
			L_{25} Grams
I	A	Slightly better	3270
	B		3270
II	C	Better	3700
	D		3270
III	E	Better	3240
	F		3150
IV	G	Worse	3180
	H		3270
V	I	Better	3600
	J		3260
VI	K	Worse	3310
	L		3590

Conclusion

The impact cutting device described in this paper is recommended for testing the cutting resistance of tread stocks because of its simplicity and the accuracy with which its results agree with road test results. The fact that the device was designed on semi-quantitative theoretical grounds gives some additional confidence in its results. It is possible that other cutting devices, designed with no regard to theory whatsoever, might operate as well as the impact device. However, it is felt that, since most laboratory tests on rubber stocks are necessarily largely empirical, it is well to attempt to design a testing machine which will operate in the ranges of the variables found in service.

Acknowledgment

The author desires to acknowledge the work of B. A. Jones, who designed the impact cutting device and performed the preliminary tests, and to thank N. Johnston and R. J. Bonstein for their helpful suggestions, and N. A. Shepard under whose direction the work was done.

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A New Plastic Material—AXF

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RUBBER technologists are familiar with the increasing number of uses to which rubber has been put in recent years through modifications and adaptations effected by skilful compounding. At the same time, however, active research has been carried out, stimulated by the desire for new materials to meet still more exacting requirements—for example, greater resistance to oils and solvents and to oxidation. In general these investigations have taken one of two directions; they have been directed to a search for new synthetic rubber-like materials or to a study of new derivatives of rubber.

In both of these fields of research, achievements of outstanding importance have been disclosed. Whitby and Katz (9) reviewed and summarized the development work on synthetic rubber from its early beginnings. The announcement of poly-chloroprene or DuPrene by Carothers (2) and his associates was soon followed by recognition that this product is a synthetic rubber-like material with physical properties not only rivaling those of rubber but superior in many particulars in which rubber is most deficient. Various olefin-polysulfide reaction products have been described by Patrick (6) and, under the trade name of Thiokols, have been presented to the industry. Other synthetic products which have attracted the attention of rubber compounders include the glyptal resins (10), flexible phenol resinoids, and the recently announced Koroseal (1). A paper by Thies and Clifford (8) has summarized the reactions of the rubber hydrocarbon, apart from oxidation and vulcanization reactions.

Method of Preparation

A new class of elastic plastic materials, recently discovered (7), is prepared by reacting ethylene dihalide in the presence of aluminum chloride with an aromatic hydrocarbon having the general formula $RC_6H_4R_1$ where R and R_1 each represent hydrogen or a saturated aliphatic hydrocarbon radical containing more than one carbon atom. Aromatic hydrocarbons with only one carbon atom in the side-chain radical (as toluene or xylene) do not undergo this reaction to give plastic products. Suitable proportions of reactants include 1 mole of aromatic compound, 1 to 3 moles of ethylene dihalide, and up to 1 mole of aluminum chloride. By suitable control the

reaction product can be varied from a very soft plastic with a shearing plasticity at 65.6° C. (150° F.) of 20 in the Mooney shearing plastometer (5) to a material having a shearing plasticity of more than 150. Products with milling, tubing, and calendering properties resembling those of rubber show a shearing plasticity in the range 40 to 80. This series of plastics has been given the designation AXF.

AXF does not react with sulfur, even after heating for an hour at 164° C. (327.2° F). This indicates the absence of aliphatic unsaturation. The structure of the products is unknown, but it seems probable that they comprise extensive chains and networks of benzene groups, each linked to at least two ethylene groups. Analysis for carbon and hydrogen shows 92.2 per cent carbon and 7.8 per cent hydrogen, and thus the empirical formula gives a 1:1 atomic ratio for carbon and hydrogen. Such a formula fits a polymer composed of $H_2C \cdot C_6H_4 \cdot CH_2$ units or of $(H_2C)_2 \cdot C_6H_2 \cdot (CH_2)_2$ units as already suggested. *sym*-Diphenylethane has been isolated as a product from the earlier stages of the reaction.

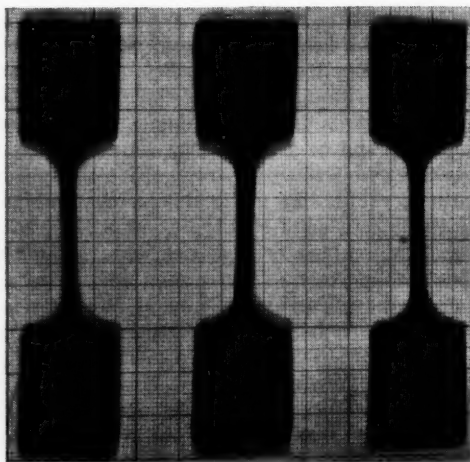


FIGURE 1. SWELLING OF AXF IN GASOLINE AND IN OIL

- A. Not immersed.
B. Immersed in gasoline 5 days at room temperature.
C. Immersed in spindle oil 5 days at 70° C.

Physical Properties

The general physical properties of AXF plastic are outlined as follows:

Specific gravity	1.04
Ash, %	1.2
Color	Dark brown
Odor	Practically none
Hardening temp., ° C.	0
Tensile strength, kg./sq. cm. (lb./sq. in.)	Up to 32 (450)
Elongation, %	Up to 600

**Action of acids and alkalis after immersion
for 1 week at room temp.:**

Concd. HCl
Concd. H_2SO_4
50% H_2SO_4
Concd. HNO_3
Glacial acetic acid
50% NaOH
 NH_4OH (30% NH_3)

No action
Swells and hardens slightly
No action
Attacked slowly
Swells moderately
No action
Surface bleached

AXF shows very low swelling in such solvents as ethyl alcohol, acetone, gasoline, kerosene, and light lubricating oils.

Figure 1 gives a comparison of a sample of AXF hydrocarbon with other AXF samples which have been immersed for

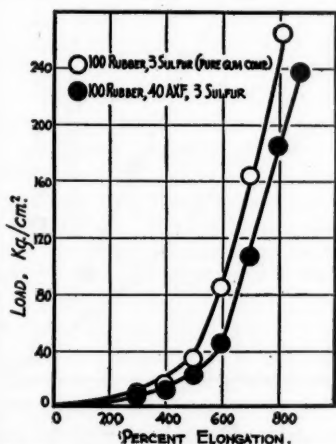


FIGURE 2. STRESS-STRAIN CURVES
FOR PURE GUM RUBBER AND FOR
AXF RUBBER

5 days in gasoline at room temperature or for 5 days in spindle oil at 70° C. There is some penetration of gasoline into the AXF as evidenced by the blister formation. The volume increase is 6.3 per cent for the sample immersed in gasoline and 3.4 per cent for the sample in oil.

On the basis of these properties, AXF has been investigated as a compounding material for use with rubber, DuPrene, or Thiokol. It will be shown that AXF may be combined with these plastics in proportions such as both to improve their processing characteristics and to give products with properties capable of withstanding more severe service conditions of certain types.

Processing Properties

Although AXF is generally used in connection with other plastics as an auxiliary compounding material, it may be of some interest to comment on its general processing properties. Grades of AXF having a Mooney shearing plasticity at 65.6° C.

(150° F.) in the range 40 to 80 may be milled, calendered, and tubed in the same manner as well broken down rubber. Similar products of greater plasticity are more tacky and handle with greater difficulty.

Compounding Material with Rubber

In Figure 2 are shown comparative stress-strain curves for a pure gum type rubber compound with 3 parts of sulfur

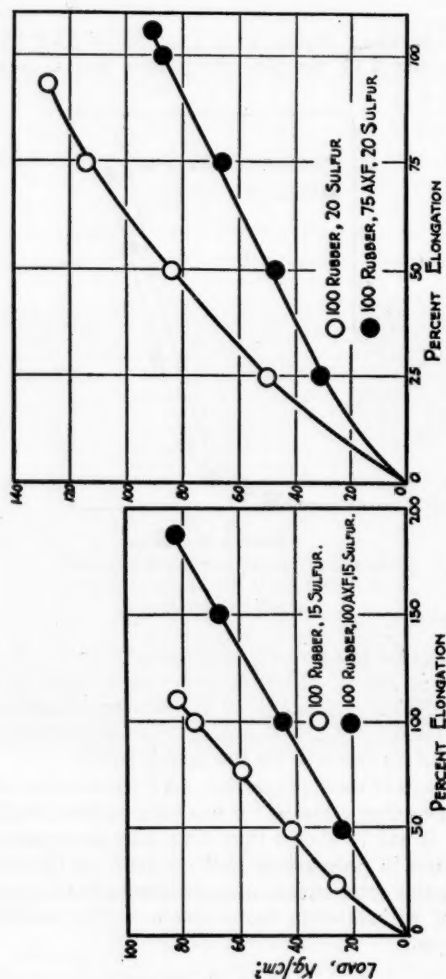


FIGURE 3. STRESS-STRAIN CURVES FOR RUBBER AND RUBBER-AXF COMPOUNDS

and for the same rubber compound with 40 parts of AXF added. The cures are for 5 minutes at 141° C. (286° F.). These curves show that the addition of this amount of AXF has but slight effect on tensile strength and ultimate elonga-

tion, and causes a small reduction in modulus. The compounding of rubber with large amounts of AXF does lower the tensile strength of the stock.

It is well known in the rubber industry that the compounding into a low-sulfur rubber stock of the various new oil-resistant synthetic rubbers has not been an effective means of developing an oil-resistant compounded rubber. AXF is accordingly not recommended as a compounding agent to promote oil resistance in a low-sulfur rubber compound. There are, however, interesting effects of AXF in low-sulfur rubber compounds. For example, a compound having rubber and AXF in the proportion 70:30 shows a reduction in rate of diffusion of air of more than 40 per cent as compared with the same compound without AXF.

A more interesting application of AXF is in the development of flexible semi-hard rubber compounds of excellent oil resistance. Rubber compounds containing 15 to 20 parts of sulfur combined per 100 of rubber are known to have high resistance to swelling in gasoline or motor oils. However, such compounds have a sufficiently low breaking elongation so that they do not meet the requirements of flexibility for many types of service. Figure 3 shows comparative stress-strain curves of semi-hard rubber compounds with and without AXF. The higher breaking elongation of the AXF stocks is to be noted, particularly in the compound with 15 parts of sulfur per 100 parts of rubber.

Figure 4 shows a comparison of the effect of gasoline immersion for a period of 3 years of a semi-hard rubber AXF compound as compared with that for a heavily loaded rubber stock designed for service as an oil-resistant compound.

Table I gives the formula for a typical AXF-rubber compound of the type under discussion and indicates the percentage swelling of this compound in gasoline and in spindle oil.

TABLE I. EFFECT OF IMMERSING SEMI-HARD RUBBER-AXF COMPOUND IN SWELLING MEDIA FOR ONE WEEK

(Cured 75 minutes at 153° C.)			
Rubber	100	Calcium oxide	10
AXF	75	Diphenyl guanidine	4
Zinc oxide	10	Sulfur	20
Carbon black	30	Antioxidant	2
Magnesium oxide	20		
Swelling Medium	Temp. of Test ° C.	Increase in Vol. %	
Motor-grade gasoline	25	32.5	
Light spindle oil	70	58.9	

The oxygen aging characteristics of rubber compounds are not changed in any substantial degree by the presence of AXF in the compound. The use of a good rubber antioxidant, in the proportions ordinarily recommended in rubber compounding, affords adequate protection.

The ozone resistance of semi-hard rubber compounds such as described in Table I, with and without AXF, was compared. Very deep cracks formed in the rubber compound while practically none appeared in the AXF-rubber compound which received the same ozone exposure.

By compounding AXF in a hard-rubber stock in a 1:1 ratio with the rubber present, it is possible to combine moder-

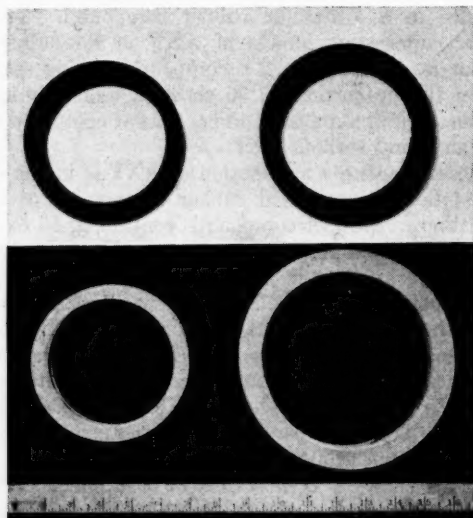


FIGURE 4. COMPARISON OF OIL-RESISTANT STOCKS

The black ring is semi-hard rubber which contains AXF; the white ring is a highly pigmented rubber compound. Left, rings as molded; right, after soaking in gasoline for 3 years.

ate flexibility with the characteristic chemical inertness of hard rubber. A typical vulcanite compound is compared with a similar stock containing 100 parts of AXF (both cured 7 hours at 145° C.):

Compound:	OD	OF
Rubber	100	100
AXF	...	100
Zinc oxide	5	5
Magnesium oxide	5	5
Sulfur	45	45
Diphenyl guanidine	4	4
Tensile strength:		
Kg./sq. cm.	476.4	176.4
Lb./sq. in.	7060	2510
Elongation at break, %	5.5	15.0

Compounding Material with DuPrene

The investigation of the behavior of AXF as a compounding material with DuPrene has had the point of view of de-

termining the possibility of improving the handling properties of the latter as well as of studying the effect upon the physical properties of the compounds. In connection with processing behavior, the milling, batch storing, calendering, and tubing properties were considered while the gasoline and oil resistance were examined carefully in connection with physical tests.

Inasmuch as factice is recommended as a processing agent for improving the handling properties of DuPrene, a number of direct comparisons of AXF and factice have been made in various types of compounds.

Figure 5 shows a comparison of the change in plasticity during storage of a DuPrene-factice compound and a DuPrene-

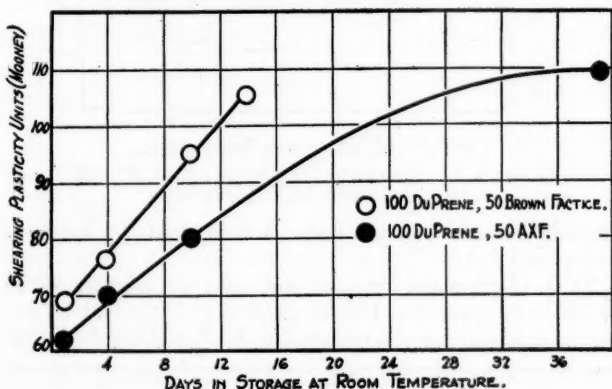


FIGURE 5. PLASTICITY CHANGES DURING STORAGE OF DUPRENE-AXF AND DUPRENE-FACTICE COMPOUNDS

AXF compound. Although the shearing plasticities of the two compounds 24 hours after mixing were 69 and 62, respectively, the DuPrene-factice compound reached a plasticity of 105 in 14 days, whereas the AXF compound required 39 days to reach a plasticity of 109. Milling tests were made daily on a sample of each compound, and the final plasticity measurements were made on the date on which the compound had so set up that it was impracticable to mill it again. Both of the stocks are conventional compounds containing both zinc oxide and magnesium oxide within the range of amounts recommended for DuPrene stocks. The compounds differ only in the presence of factice or AXF.

The excellent plasticizing action which AXF shows in DuPrene stocks reduces the temperatures developed during milling, promotes smoothness of finish of calendered stocks, reduces calender shrinkage, and improves the tubing properties.

Figures 6 and 7 show the effects on gasoline and oil resistance of a typical DuPrene oil-resistant compound which may be

obtained by partial substitution of AXF for DuPrene. The DuPrene compound (D-1) used in this study has been described by Hayden and Krismann (4). The 70 DuPrene-30 AXF compound shows approximately 30 per cent lower

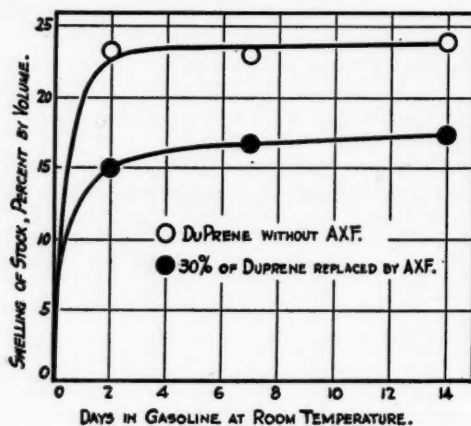


FIGURE 6. GASOLINE SWELLING OF DUPRENE AND DUPRENE-AXF COMPOUND

swelling in both gasoline and oil than does the DuPrene Compound D-1.

Table II gives the formulas and some physical properties of DuPrene compound D-1, a modified D-1 in which 30 per cent of the DuPrene was replaced by AXF, and another modi-

TABLE II. DATA ON OIL-RESISTANT COMPOUNDS
[Cured 45 minutes at 141.7° C. (287° F.)]

	DuPrene D-1	Modified DuPrene D-1 Fillers replaced by AXF	70 DuPrene- 30 AXF
Formulas			
DuPrene	100	100	70
AXF	...	52	30
Whiting	85	...	85
Gastex ^a	28.5	...	28.5
Glue	11.5	11.5	11.5
Zinc oxide	10	10	10
Light-calcined magnesia	10	10	10
Cottonseed oil	2	2	2
Wood Neosone rosin	5	5	5
Neosone D ^b	2	2	2
Sulfur	1.5	1.5	1.5
Properties Unaged			
Tensile strength:			
Kg./sq. cm.	91.4	98.1	72.9
Lb./sq. in.	1301	1395	1035
Max. elongation, %	410	740	250
Set, %	19	45	17
Properties after 5-Day Immersion in Spindle Oil at 70° C.			
Tensile strength:			
Kg./sq. cm.	74.5	53.4	50.4
Lb./sq. in.	1060	759	716
Max. elongation, %	370	750	210
Set, %	10	16	7
Swelling, % by vol.	45.4	49.6	33.7

^a A special variety of carbon black.

^b Phenyl-β-naphthylamine.

fication of D-1 in which all of the fillers were replaced by an equal volume of AXF.

Figure 8 shows the stress-strain curves for the series of compounds described in Table II—namely, DuPrene oil-resistant compound D-1, a similar compound in which all of the fillers have been replaced by an equal volume loading of AXF, and another compound in which partial substitution (30 parts by weight) of AXF has been made for an equivalent amount of DuPrene. The replacement of fillers by AXF gives a compound of higher volume cost, but offers the possibility of combining the features of high breaking elongation with excellent resistance to gasoline and oil.

Figure 9 compares the swelling changes after 5 days of immersion in spindle oil at 70° C. of a DuPrene-AXF and a DuPrene-factice compound. The dimensions of the test sample before immersion are also shown for comparison. The DuPrene-factice compound is based on compound 236¹ described in the DuPrene Manual (3). The formulas are as follows:

	DuPrene-Factice	DuPrene-AXF
DuPrene	100	100
Soft brown factice (hardness 10)	150	
AXF		150
Thermax ^a	370	370
Zinc oxide	10	10
Light-calcined magnesia	10	10
Rosin	1	1
Soft cumar ^b	10	10
Cottonseed oil	5	5
Neosone D	2	2

^a A special variety of carbon black.

^b *p*-Coumarone resin.

TABLE III. PHYSICAL TESTS OF AXF IN DUPRENE COMPOUNDS

Formula of Compound BP									
DuPrene	60	Sulfur							0.5
AXF	40	Cottonseed oil							2
Light-calcined magnesia	5	Neosone D							2
Zinc oxide	5	Carbon black							42.8
		Wood rosin							5
Tensile Strength									
Cure at 141.7° C.	Unaged		96 Hr. in Oxygen at 70° C.		1 Week in Gasoline at Room Temp.		1 Week in Spindle Oil at 70° C.		
	Kg./ sq. cm.	Lb./ sq. in.	Kg./ sq. cm.	Lb./ sq. in.	Kg./ sq. cm.	Lb./ sq. in.	Kg./ sq. cm.	Lb./ sq. in.	
15	112.1	1595	106.9	1520	108.3	1540	78.8	1120	
30	115.8	1645	109.7	1560	111.8	1590	79.5	1130	
45	116.8	1660	110.4	1570	111.1	1580	80.2	1140	
60	119.5	1700	109.7	1560	113.9	1620	80.9	1150	
75	116.8	1660	112.5	1600	106.2	1510	80.9	1150	
90	117.4	1670	102.0	1450	108.3	1540	85.2	1210	
Maximum Elongation, Per Cent									
15	330		250		310		310		
30	330		240		300		300		
45	320		230		290		290		
60	320		230		300		290		
75	290		240		270		280		
90	310		220		280		280		

¹ This particular compound modification was suggested by a member of the development staff of the Rubber Chemicals Division of E. I. du Pont de Nemours & Company, Inc.

The use of AXF in DuPrene is not recommended where the highest tensile strength and abrasion resistance are required. Tests have shown no evidence that either the oxygen or heat-aging of DuPrene compounds is impaired by the presence of AXF. There is evidence that the high ozone resistance of DuPrene is enhanced when AXF is added to a DuPrene compound.

DuPrene-AXF compounds show higher tensile strengths as the carbon black loading is increased. In a 60 DuPrene-40 AXF stock, as the volume loading of carbon black is increased from 20 to 40 volumes on 100 volumes of DuPrene-AXF plastic,

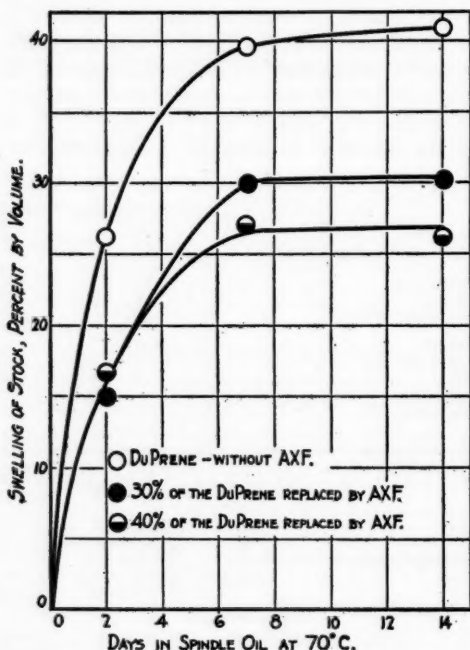


FIGURE 7. OIL SWELLING OF DUPRENE AND DUPRENE-AXF COMPOUND

the tensile rises from approximately 100 to 150 kg. per square cm.

Table III shows several physical properties over a range of cures of a typical DuPrene-AXF compound loaded with carbon black.

AXF has also been found very resistant to the action of lithographic varnishes. The swelling of AXF in a commercial lithographic varnish after 5 days' immersion amounted to only 1.5 per cent. This feature has been used to advantage in compounding with DuPrene to prepare products which are particularly adapted to use in printers' blankets and inking rollers for some types of work.

Compounding Material with Thiokol

Some studies on the effect of compounding AXF with the several commercial olefin polysulfide plastics have been made. With certain types of these plastics, it has been recommended that small percentages of rubber be added to assist in processing operations.

It has been found that amounts of AXF as high as 20 per cent by weight may be compounded into these plastics to give products more readily processed, with somewhat higher

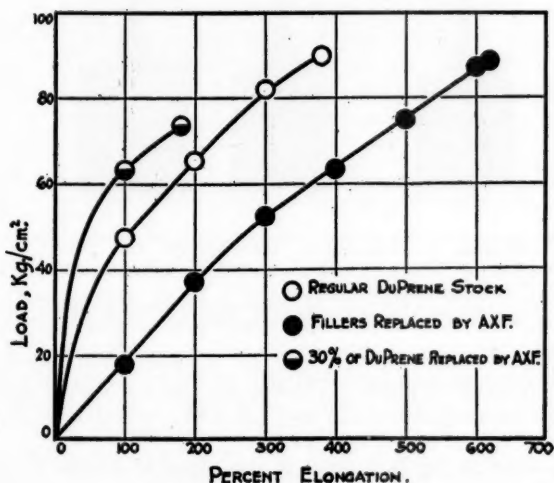


FIGURE 8. STRESS-STRAIN CURVES OF DUPRENE AND DUPRENE-AXF COMPOUNDS

breaking elongation and the same high resistance to gasoline and oils characteristic of the olefin polysulfide plastics when processed alone. Table IV shows the physical properties of several Thiokol compounds with rubber and with AXF.

A new type of olefin polysulfide plastic recently introduced (Thiokol D) is highly resistant to mill breakdown. It has been found that the introduction of approximately 20 parts by weight of AXF to 100 parts of Thiokol plastic effects a reduction in milling time of a standard Thiokol D compound from 40 to 15 minutes for a 500-gram mix on a laboratory mill.

AXF reduces the shearing plasticity of Thiokol, as shown by the following data:

	Milling Time, Minutes	Mooney Plasticity Units at 100° C. (212° F.)
Standard Thiokol D	40*	172
Thiokol D + 10 AXF	15	126
Thiokol D + 20 AXF	15	81

* The longer milling time with the standard Thiokol D compound was necessary to get the mix into sheet form.

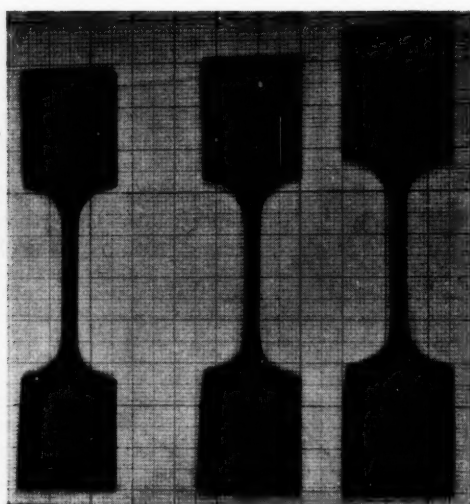


FIGURE 9. SWELLING RESISTANCE OF DUPRENE-FACTICE AND DUPRENE-AXF COMPOUNDS

- A. Test sample, not immersed.
 B. DuPrene-AXF, immersed in spindle oil 5 days at 70° C.
 C. DuPrene-factice, immersed in spindle oil 5 days at 70° C.

Table V shows the test data for a typical compounded olefin polysulfide plastic (Thiokol D) and for similar compounds to which 10 and 20 parts of AXF, respectively, were added.

No attempt has been made in this paper to discuss all the possible applications of AXF as a compounding material. It is desired to point out that the process for preparing the

TABLE IV. AXF VS. RUBBER IN THIOKOL A COMPOUNDS
 (Cured 60 minutes at 141° C.)

Formula	BQ	BR	CY
Olefin polysulfide plastic, Thiokol A	100	100	100
Rubber	5	20	...
AXF	20
Diphenylguanidine	0.25	0.25	0.25
Tetramethylthiuram disulfide	0.10	0.10	0.10
Zinc oxide	10	10	10
Stearic acid	0.5	0.5	0.5
Properties, Unaged			
Tensile strength:			
Kg./sq. cm.	53.7	60.6	49.0
Lb./sq. in.	764	862	697
Max. elongation, %	220	350	290
Set, %	20	52	43
Immersed 7 Days in Gasoline at Room Temperature			
Tensile strength:			
Kg./sq. cm.	50.5	48.8	46.2
Lb./sq. in.	718	694	657
Max. elongation, %	220	290	270
Set, %	22	26	35
Vol. increase, %	0.0	25.8	0.0
Immersed 7 Days in Spindle Oil at 70° C.			
Tensile strength:			
Kg./sq. cm.	47.7	43.8	42.8
Lb./sq. in.	678	623	608
Max. elongation, %	200	240	230
Set, %	20	22	24
Vol. increase, %	1.2	29.5	0.0

TABLE V. EFFECT OF AXF IN THIOKOL D COMPOUNDS
(Cured 30 minutes at 141° C.)

Formula	OH	NZ	OA
Olefin polysulfide plastic, Thiokol D	100	100	100
AXF	...	10	20
Gastex	55	55	55
Zinc oxide	10	10	10
Stearic acid	0.5	0.5	0.5
Altax (benzothiazyl disulfide)	0.3	0.3	0.3
Properties, Unaged			
Tensile strength:			
Kg./sq. cm.	72.3	60.7	52.2
Lb./sq. in.	1027	864	742
Max. elongation, %	450	470	480
Set, %	17	18	19
Immersed 7 Days in Gasoline at Room Temperature			
Tensile strength:			
Kg./sq. cm.	46.5	54.0	40.6
Lb./sq. in.	660	768	577
Max. elongation, %	460	510	520
Set, %	20	25	34
Vol. increase, %	2.1	2.2	2.8
Immersed 7 Days in Spindle Oil at 70° C.			
Tensile strength:			
Kg./sq. cm.	32.7	45.4	33.0
Lb./sq. in.	464	646	469
Max. elongation, %	420	520	530
Set, %	21	23	31
Vol. increase, %	1.4	2.8	2.8

material has been brought under such control as to make possible the preparation of a type of material with uniform physical properties but capable of controlled variation as to hardness and viscosity. The material has been found to have interesting properties as a plasticizing agent and as a stabilizing agent for compounded DuPrene in storage. It also has distinct possibilities as a processing agent for polysulfide plastics and enhances some of their useful properties.

More recent investigations which have not yet been concluded suggest that AXF may find important application in the wire insulation field. These features of AXF application include improvements in the oil and solvent resistance of cable coverings, and the still more important property of high resistance to electrical breakdown. Details of these developments will be reserved until such time as a more complete quantitative study has been made.

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CORRECTION

Investigations of Dispersing Agents and Stabilizing Agents for Latex Mixtures, and the Behavior of Latex Mixtures when Stored

Otto Bächle

On page 256 of the April issue the sentence commencing on the fourth line below Table V should read as follows:

It follows therefore that for good dispersion and at the same time good resistance to coagulation, the concentration of stabilizing agent must be above a certain minimum value, which, as is evident from the facts above, depends on the kind and quantity of the agent.